The Boeing Company
Santa Susana Field Laboratory
5800 Woolsey Canyon Road
Canoga Park, CA 91304-1148

Certified Mail

June 1, 2009
In reply refer to SHEA-108736

Mr. Norman Riley
Project Director
California Department of Toxic Substances Control
1001 "I" Street
P. O. Box 806
Sacramento, California 95812-0806

RE: Treatability Study Workplans
Santa Susana Field Laboratory
Ventura County, California

Dear Mr. Riley:

Pursuant to the draft schedule for corrective action developed in accordance with the August 2007 Consent Order for Corrective Action, Boeing is submitting the attached Feasibility Study Workplan, Santa Susana Field Laboratory, prepared by MWH and dated April 2009. This document is submitted on behalf of the Boeing Company, the Department of Energy, and the National Aeronautics and Space Administration as described in the Feasibility Study Workplan submitted on April 21, 2009.

Please address any questions regarding this workplan to Mr. David Dassler at (661) 210-5673.

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

Signature: _____
Name: Thomas D. Gallacher
Director, Santa Susana Field Laboratory
Title: Environment, Health and Safety
Date: 6/1/2009

cc: Distribution

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# TREATABILITY STUDY WORK PLANS
# SANTA SUSANA FIELD LABORATORY

## VENTURA COUNTY, CALIFORNIA

**Prepared For:**

**The Boeing Company**
**The National Aeronautics and Space Administration**
**The United States Department of Energy**

**Prepared By:**

**MWH**
**2121 North California Blvd.**
**Suite 600**
**Walnut Creek, California 94596**

**June 2009**

MWH

## PROFESSIONAL CERTIFICATION
## TREATABILITY STUDY WORK PLANS

These work plans have been prepared by a team of qualified professionals under the supervision of the senior staff whose seal and/or signatures appear below.

Christopher Cain, P.E. C29003

Richard G. Andrachek, P.E.

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## LIST OF ACRONYMS AND ABBREVIATIONS

| | |
|---|---|
| bgs | below ground surface |
| BVE | Bedrock Vapor Extraction |
| cDCE | cis-1,2-dichloroethene |
| DTSC | California Department of Toxic Substances Control |
| FS | Feasibility Study |
| IEL | Instrument and Equipment Laboratory |
| RI | Remedial Investigation |
| SSFL | Santa Susana Field Laboratory |
| TCE | trichloroethene |
| VOCs | volatile organic compounds |

# 1.0 INTRODUCTION

A feasibility study (FS) work plan for the Santa Susana Field Laboratory (SSFL) was delivered to the California Environmental Protection Agency, Department of Toxic Substances Control (DTSC) on April 21, 2009 (MWH, 2009). The FS work plan described the methodology for identifying, developing, and evaluating remedial action alternatives for constituents in media of concern at the SSFL. The SSFL is located in southeastern Ventura County about 29 miles northwest of downtown Los Angeles, California as shown in Figure 1. The FS work plan stated that treatability study work plans would be submitted for four technology studies by June 2, 2009. This document summarizes and presents the work plans for conducting treatability studies for each of the four technologies identified in the FS work plan.

The four technologies include:

- Vapor extraction in the unsaturated bedrock
- *In situ* chemical oxidation,
- Enhanced biological reduction, and
- Thermal treatment.

Background information and the basis for selecting these technologies for treatability studies are provided in the FS work plan (MWH, 2009) and are incorporated into this document by reference. The FS work plan stated that the potential effectiveness, implementability, and cost of chemical oxidation as a groundwater remediation technology should be evaluated in the field, while enhanced biological reduction and thermal treatment were proposed for further evaluation as to their potential effectiveness using laboratory experiments. A brief description of each technology experiment is provided in the following sections and work plans for conducting each of the four technology treatability studies are provided in appendices.

## 2.0 BEDROCK VAPOR EXTRACTION FIELD EXPERIMENT

A field experiment for evaluating bedrock vapor extraction (BVE) of volatile organic compounds (VOCs) is proposed for in the unsaturated Chatsworth formation[1] to assess its potential applicability as a technology that could achieve target remedial action objectives. Vapor extraction is a well-established treatment technology for the remediation of VOCs in contaminated soil (i.e., unlithified sediments), but its effectiveness, implementability and cost in fractured sedimentary bedrock settings like the Chatsworth formation are not well established. The conditions influencing the transport and fate of VOCs in the vadose zone Chatsworth formation were evaluated and used to establish performance criteria for the bedrock vapor extraction field experiment. Performance criteria for the BVE field experiment include evaluating the: production of air from an extraction well(s); vacuum response in fractures and in rock matrix blocks; effects of lithology changes and/or structural features on the advective flow paths in the formation; VOC mass flow rate over time; and the diffusive response of VOCs from the rock matrix blocks post-treatment.

A site was selected for the BVE field experiment from one of 11 source locations across the SSFL where rock core samples have been collected throughout the vadose zone bedrock and analyzed for the occurrence and distribution of VOCs. Each was evaluated as a candidate for the BVE field experiment. The criteria considered in ranking and selecting a location for the field experiment are: the VOC mass and distribution in the vadose zone; site accessibility; vadose zone thickness; and general characterization information to support design of the field experiment. Considerations of the VOC mass in the vadose zone included both the total mass present in the unsaturated zone, its vertical distribution, and operational usage related to the projected VOC releases that may have occurred.

The area in the vicinity of corehole C-4 at the Bowl RI site was selected for the BVE field experiment. The location is shown in Figure 2. The thickness of the vadose zone here is about 90 feet and there are appreciable detections of TCE and its daughter products throughout the

[1] The Chatsworth formation is a deep-sea turbidite formation composed primarily of sandstone with interbeds of siltstone and shale, and is the primary geologic unit that underlies nearly all of the SSFL. It strikes N70$^{o}$E and dips about 25$^{o}$ to 30$^{o}$ to the northwest within the SSFL. A number of faults and deformation bands are present within and adjacent to the facility, nearly all of which dip steeply.

vertical profile. The area is readily accessible for the placement of equipment and test infrastructure. The area is also well-characterized as to the geologic framework and the effects, if any, of different geologic features on BVE system design and performance can be evaluated. Finally, the Bowl Remedial Investigation (RI) site has been previously reported to be a location where a considerable mass of TCE entered the subsurface (CH2MHill, 1993).

A work plan for implementing the bedrock vapor extraction field experiment at the Bowl RI site is provided in Appendix A.

## 3.0 CHEMICAL OXIDATION FIELD EXPERIMENT

A field experiment for evaluating *in situ* chemical oxidation of chlorinated ethenes is proposed because it offers the potential for more accurately assessing the effectiveness of delivering and distributing fluids into fractured bedrock beneath the selected test location at the SSFL. Fluid delivery to impacted subsurface media is most often the factor that limits the effectiveness of an *in situ* mass transformation technology. Assuming excess oxidant is injected, one advantage of using an oxidant such as potassium or sodium permanganate is its characteristic color that allows for an evaluation of its arrival and distribution by visual inspection. This characteristic also applies to its infiltration into the bedrock matrix by diffusion. Additionally, these oxidants are stable and persistent in the groundwater system, can be delivered efficiently at relatively high concentrations, and their potential arrival and distribution can be monitored through the collection of general groundwater parameters such as specific conductivity. Data from the field experiment can be evaluated relative to the theoretical effectiveness of diffusing oxidants by applying analytical or numerical solutions or numerical models. This type of information can be used to assess and compare what can be expected in the field to theoretical results, estimate relative technology efficiencies, and apply more realistic estimates of key parameters during preparation of the FS.

Seven characteristics were identified as a means of evaluating the suitability of various areas of impacted groundwater for a chemical oxidation field experiment. Impacted groundwater at the Instrument and Equipment Laboratory (IEL) RI Site in the northeastern portion of the SSFL (see

Figure 2 for location) is given the highest preference as a field experiment site for the following reasons:

- The existence of primarily chlorinated ethenes in the groundwater north of the IEL fault,
- The availability of a large amount of data describing the distribution and concentration of chlorinated ethenes in the bedrock matrix,
- The existence of an effective horizontal and vertical monitoring network,
- Its relatively distant position from property boundaries or seeps, and
- The field experiment may yield additional insights into the groundwater flow system across and/or along faults in this area of the site.

Subsurface characteristics that are less than optimal at this site are the higher bulk hydraulic conductivity values in local bedrock than most other areas of the SSFL and geochemical conditions that are potentially conducive to complete biologically-mediated reductive dechlorination of the chlorinated ethenes. The higher bulk hydraulic conductivity at the site is predicted to produce results regarding oxidant delivery and distribution that appear to be more favorable than will be the case at many other locations at the SSFL. Introduction of a chemical oxidant at this location is predicted to change the local geochemical conditions such that natural reductive dechlorination processes may be negatively impacted.

A work plan for implementing the *in situ* chemical oxidation field experiment at the IEL RI Site is provided in Appendix B.

## 4.0 ENHANCED BIOLOGICAL REDUCTION EXPERIMENT

Enhanced biological reduction is proposed for further laboratory testing because additional assessment is required as to whether the Chatsworth formation is conducive to biostimulation (i.e., increasing the growth rate of the native organisms) and potentially bioaugmentation (i.e., adding exogenous bacteria subsequent to and along with energy sources and nutrients).

Results of laboratory experiments conducted to date on select samples of SSFL rock indicate that the microorganism identified as being responsible for transforming trichloroethene (TCE) to cis-1,2-dichlorothene (cDCE) has limited capacity to further transform cDCE. SSFL field studies conducted to date on potential TCE degradation report the stalling of TCE transformation at cDCE within certain areas of the site, which appears to support the findings of laboratory experiments conducted by Clemson University. The field studies also indicate that geochemical conditions in certain areas of the SSFL are not sufficiently reducing to support large populations of microbes known to completely transform chlorinated ethenes (i.e. *Dehalococcoides*) without the addition of electron donors to lower the reduction-oxidation potential. Results from other field studies in progress show the presence of dissolved gases that are indicative of the complete transformation of chlorinated ethenes. Additional studies are underway in laboratories at the University of Guelph that evaluate the potential presence and composition of microorganisms in the rock matrix that may be transforming chlorinated ethenes. The plan for guiding these studies is provided in Appendix C.

In addition to reductive dechlorination, a combination of abiotic and biotic transformation processes may be a significant fate process for chlorinated ethenes at SSFL. It has been speculated that iron-containing minerals in the Chatsworth sandstone are responsible for the abiotic transformation of cDCE and TCE; microbes then complete the transformation by oxidizing the products to $CO_2$. In experiments conducted to date, however, the extent of transformation was limited to approximately 25 percent or less of the cDCE. The reason for this limitation was not evaluated. One possibility is that the transformation capacity of the minerals was due to a lack of reductant that may be required to re-reduce them to an active state. A growing body of evidence suggests that abiotic transformation of chlorinated ethenes can be facilitated by producing low redox conditions and biostimulation can be a cost-effective way of achieving this.

Therefore, laboratory experiments need to evaluate the potential effectiveness of different electron donors in stimulating increases in the population of existing microorganisms and the potential resultant affect of enhancing the transformation rate. Rock core samples needed for the experiments will be obtained from a combination of coreholes C-12, C-13, C-14 and/or C-15, the

locations of which are shown in Figure 2. The studies underway at the University of Guelph as outlined in Appendix C and those proposed as described in Appendix D should provide complimentary data that allow for a robust evaluation to be made as to the effectiveness, implementability and cost of enhanced biological reduction of chlorinated ethenes in the FS.

A subsequent study may be performed to assess the potential for supporting and stimulating the growth of exogenous bacteria (i.e., bioaugmentation). Performance of this study will be dependent upon the results from the microbial characterization and biostimulation work and from other information currently being compiled for the site-wide groundwater remedial investigation report to be submitted in late September 2009.

A work plan for implementing the enhanced biological reduction experiment is provided in Appendix D.

## 5.0 THERMAL TREATMENT EXPERIMENT

While most thermal systems to date have operated within or just below the vadose zone at depths to 100 feet or so below ground surface (bgs), the SSFL is characterized by the presence of contamination at depths up to 900 feet bgs, hundreds of feet below the water table. The performance of thermal treatment under these conditions is not well documented. While it may be technically possible to dewater a particular SSFL RI site to conduct a full scale thermal treatment at depths to 500 feet bgs, it would not be feasible to do so at a pilot scale. It would be very advantageous to be able to determine if thermal treatment technology can be effective without fully dewatering a site. Therefore, laboratory experiments will be conducted to evaluate the extent to which heating increases diffusion and transformation as opposed to vaporization under this operational scenario. Rock core samples needed for the experiments will be obtained from corehole C-15, located with the Delta RI site as shown in Figure 2.

The evaluation of thermal treatment as a potential full-scale remedial technology for SSFL can be supported by the use of: results from characterization studies of subsurface conditions completed to date, results of past pilot-scale and full-scale thermal applications at other sites, calculations, and evaluation of expected performance in comparison to other technologies.

Estimates as to the energy required, which is directly related to mass removal efficiency, could be determined with experimental data using SSFL rock matrix samples. It is proposed that this uncertainty be evaluated by conducting laboratory experiments designed to characterize the level to which heating would enhance mass removal from the bedrock matrix. The combination of the laboratory test results and other factors, as described above, will support the full evaluation of the application of thermal remediation technologies at the SSFL.

A work plan for implementing the thermal treatment experiment is provided in Appendix E.

## 6.0 SUMMARY AND SCHEDULE

Four treatability studies are being proposed in support of the feasibility study for the SSFL (MWH, 2009). One treatability study is being proposed to collect data to evaluate the effectiveness, implementability and cost of extracting organic vapors (i.e., VOCs) from the vadose zone of the Chatsworth formation bedrock that underlies the SSFL. The vadose zone source at the Bowl RI site has been selected as the location for conducting this technology evaluation in the field.

Three treatability studies are being proposed to collect data to evaluate the effectiveness, implementability and cost of treating groundwater in the Chatsworth formation and include:

- *In situ* chemical oxidation at the IEL RI site,
- A laboratory treatability study of enhanced biological reduction and a second laboratory treatability study of thermal treatment. Samples needed to conduct these treatability studies will be obtained from one or more of four coreholes that have been drilled at the SSFL.

A summary project schedule for performing the four treatability studies is shown in Figure 3. Major activities include review, revision and approval of this work plan by DTSC and the performance of each of the four studies. As currently conceived, the enhanced biological reduction laboratory experiment has the longest duration as the biological stimulation of

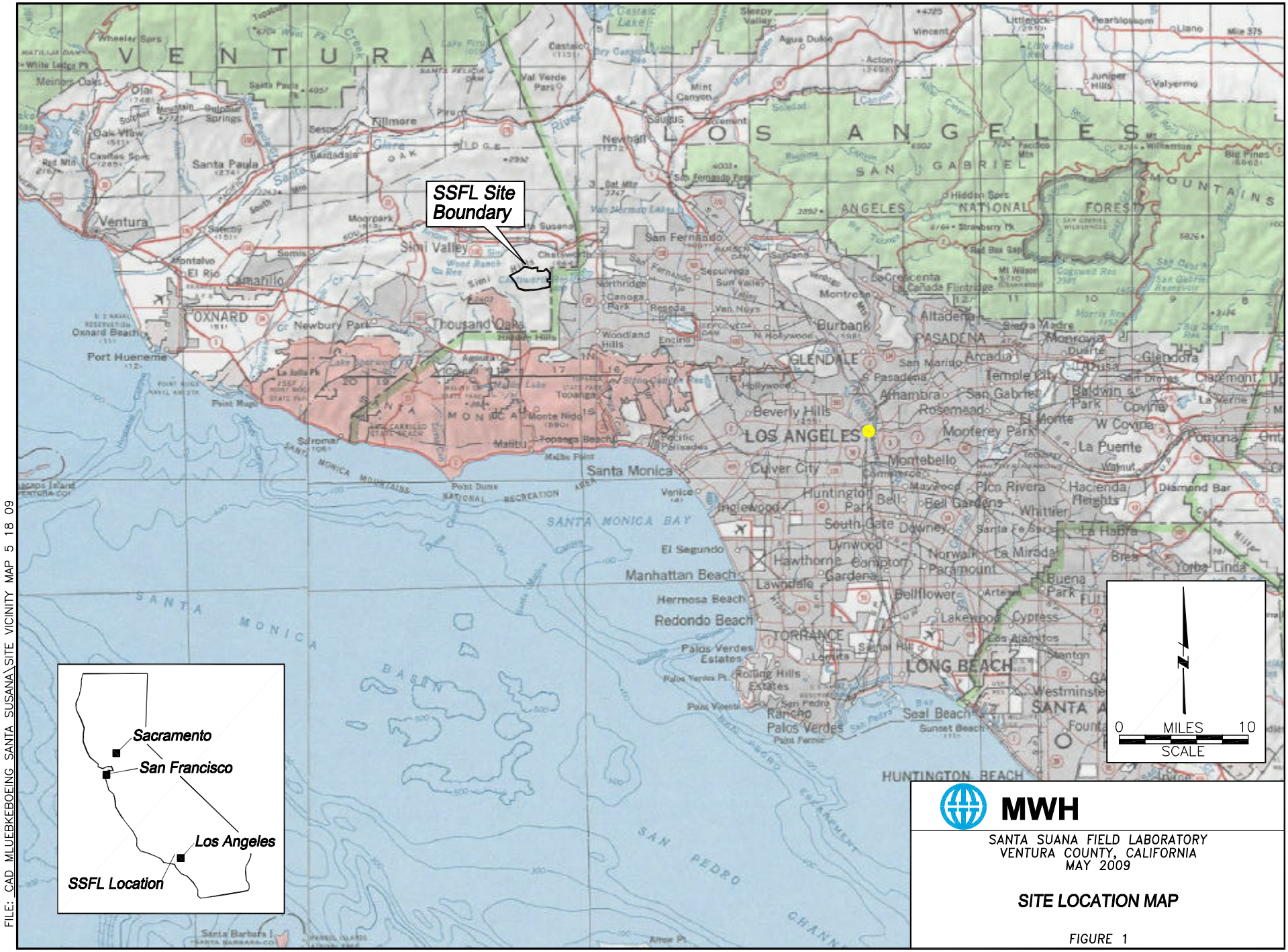
indigenous bacteria requires sufficient time to enhance population growth and/or colonize the samples and then grow. The activities, durations and dependencies of the three other treatability studies are projected to take less time than the enhanced biological studies. All four studies are projected to be completed such that the data produced from the studies can be used during conductance of the feasibility study for the SSFL.

## 7.0 REFERENCES

CH2MHill, 1993. Records Search and Trichloroethylene Release Assessment for Santa Susana Field Laboratory, Ventura County, California, Volumes 1 and 2. June.

MWH, 2009. Feasibility Study Work Plan, Santa Susana Field Laboratory, Ventura County, California. April.

**FIGURES**

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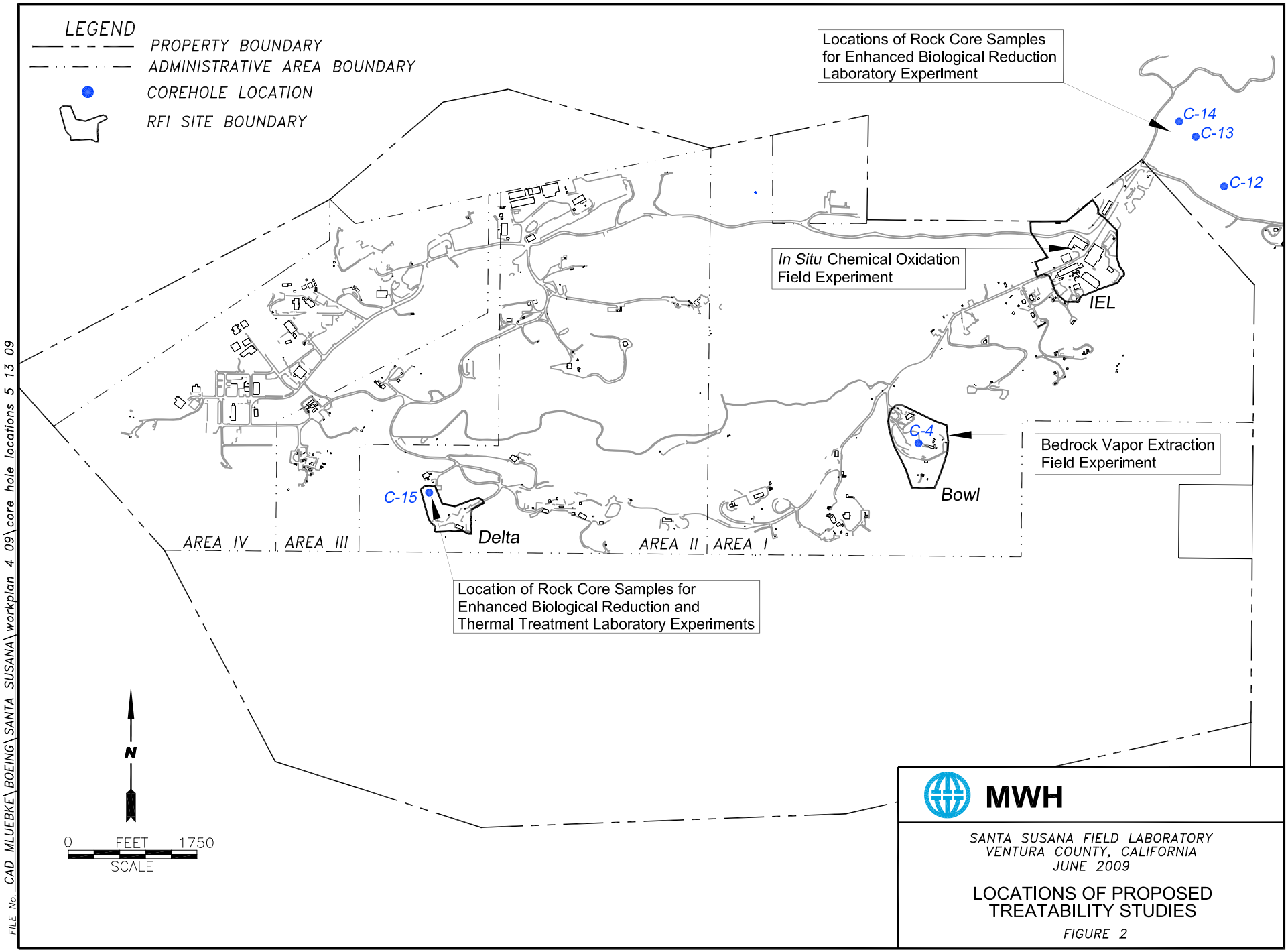


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MWH

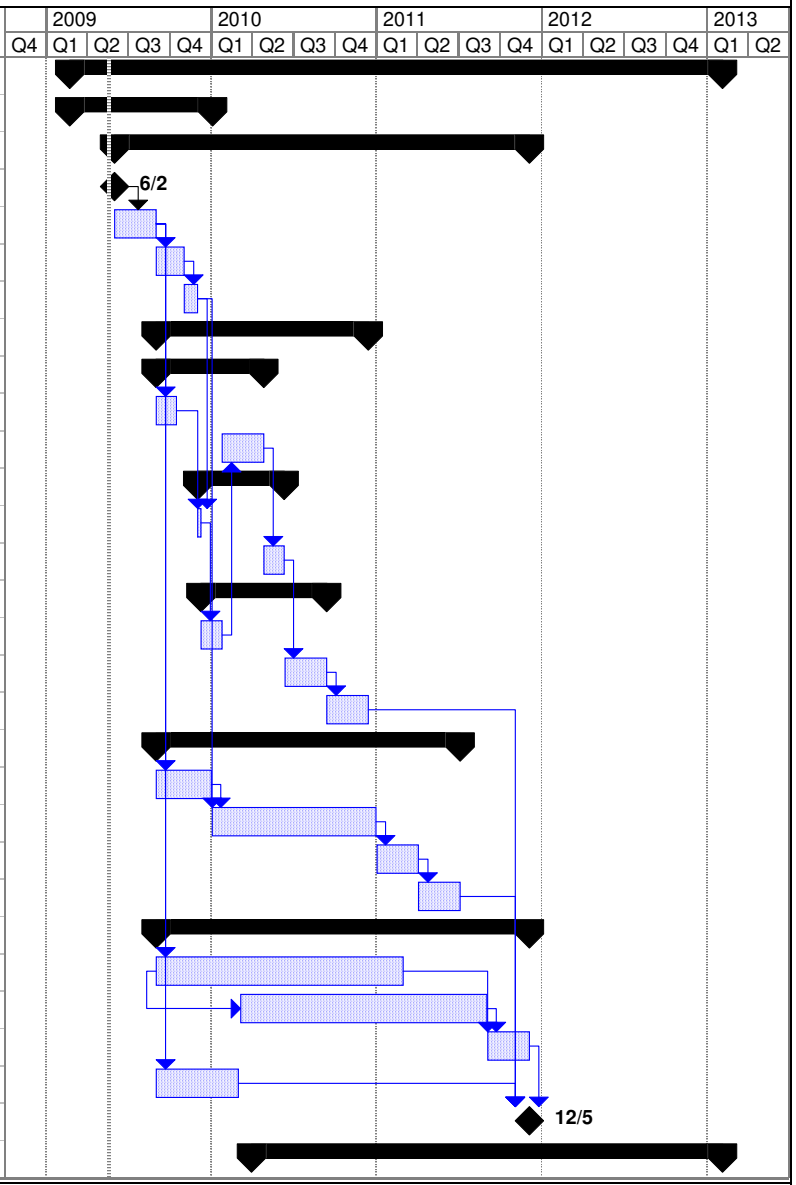
SANTA SUSANA FIELD LABORATORY
VENTURA COUNTY, CALIFORNIA
JUNE 2009

# LOCATIONS OF PROPOSED TREATABILITY STUDIES

FIGURE 2

**Figure 3**
**Schedule, SSFL Treatability Studies**

| ID | Task Name | Duration | Start | Finish |
|---|---|---|---|---|
| 1 | **Feasibility Study** | **1031 days?** | **Mon 2/23/09** | **Mon 2/4/13** |
| 2 | **FS Work Plan** | **226 days** | **Mon 2/23/09** | **Mon 1/4/10** |
| 12 | **Treatability Studies** | **655 days?** | **Tue 6/2/09** | **Mon 12/5/11** |
| 13 | Submit TS Work Plans | 0 days | Tue 6/2/09 | Tue 6/2/09 |
| 14 | DTSC review | 66 days | Tue 6/2/09 | Tue 9/1/09 |
| 15 | Revise/update work plan(s) | 44 days | Wed 9/2/09 | Mon 11/2/09 |
| 16 | DTSC final review & approval | 22 days | Tue 11/3/09 | Wed 12/2/09 |
| 17 | **Bedrock Vapor Extraction Field Experiment** | **335 days?** | **Wed 9/2/09** | **Tue 12/14/10** |
| 18 | **Infrastructure & permitting** | **170 days** | **Wed 9/2/09** | **Tue 4/27/10** |
| 19 | Phase 1 | 33 days | Wed 9/2/09 | Fri 10/16/09 |
| 20 | Phase 2 | 66 days | Tue 1/26/10 | Tue 4/27/10 |
| 21 | **Operations** | **137 days?** | **Thu 12/3/09** | **Fri 6/11/10** |
| 22 | Phase 1 | 5 days | Thu 12/3/09 | Wed 12/9/09 |
| 23 | Phase 2 | 33 days? | Wed 4/28/10 | Fri 6/11/10 |
| 24 | **Post-test sampling/ data reduction** | **198 days** | **Thu 12/10/09** | **Mon 9/13/10** |
| 25 | Phase 1 | 33 days | Thu 12/10/09 | Mon 1/25/10 |
| 26 | Phase 2 | 66 days | Mon 6/14/10 | Mon 9/13/10 |
| 27 | Performance reporting | 66 days | Tue 9/14/10 | Tue 12/14/10 |
| 28 | **Chemical Oxidation Field Experiment** | **480 days** | **Wed 9/2/09** | **Tue 7/5/11** |
| 29 | Infrastructure & permitting | 88 days | Wed 9/2/09 | Fri 1/1/10 |
| 30 | Operations | 260 days | Mon 1/4/10 | Fri 12/31/10 |
| 31 | Post-test sampling | 66 days | Mon 1/3/11 | Mon 4/4/11 |
| 32 | Performance reporting | 66 days | Tue 4/5/11 | Tue 7/5/11 |
| 33 | **Enhanced Bio Reduction Lab Experiment** | **589 days** | **Wed 9/2/09** | **Mon 12/5/11** |
| 34 | Batch microcosms | 390 days | Wed 9/2/09 | Tue 3/1/11 |
| 35 | Biostimulation in continuous flow columns | 390 days | Mon 3/8/10 | Fri 9/2/11 |
| 36 | Reporting | 66 days | Mon 9/5/11 | Mon 12/5/11 |
| 37 | Thermal Treatment Lab Experiment | 130 days | Wed 9/2/09 | Tue 3/2/10 |
| 38 | Treatability studies complete | 0 days | Mon 12/5/11 | Mon 12/5/11 |
| 39 | **FS Report** | **743 days** | **Thu 4/1/10** | **Mon 2/4/13** |




Task
Split
Progress
Milestone
Summary
Project Summary
External Tasks
External Milestone
Deadline

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# TREATABLILITY STUDY WORK PLANS
# SANTA SUSANA FIELD LABORATORY
# VENTURA COUNTY, CALIFORNIA

## *APPENDIX A*
## *BEDROCK VAPOR EXTRACTION FIELD EXPERIMENT WORK PLAN*

**Prepared For:**

**THE BOEING COMPANY**
**The NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
**and**
**The UNITED STATES DEPARTMENT OF ENERGY**

**Prepared By:**

**MWH**
**618 Michillinda Avenue Suite 200**
**Arcadia, CA 91007**

**June 2009**

# WORK PLAN
# BEDROCK VAPOR EXTRACTION FIELD EXPERIMENT
# SANTA SUSANA FIELD LABORATORY

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**VENTURA COUNTY, CALIFORNIA**

**Prepared For:**

**The Boeing Company**
**The National Aeronautics and Space Administration**
**The United States Department of Energy**

**Prepared By:**

**MWH**
**2121 North California Blvd.**
**Suite 600**
**Walnut Creek, California 94596**

**June 2009**

MWH

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A TCE and Other Select VOC Porewater Profiles

## LIST OF ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| AC | asphaltic concrete |
| atm | atmosphere |
| bgs | below ground surface |
| Boeing | The Boeing Company |
| BVE | Bedrock Vapor Extraction |
| CFC-113 | chlorofluorocarbon-113 |
| $cm^2$ | square centimeters |
| CTL | Components Test Laboratory |
| DCE | dichloroethene |
| DNAPL | dense non-aqueous phase liquid |
| DOE | United States Department of Energy |
| EPA | Environmental Protection Agency |
| FS | feasibility study |
| FSDF | Former Sodium Disposal Facility |
| $g/m^2$ | grams per square meter |
| IEL | Instrument and Equipment Laboratory |
| mg/L | milligrams per liter |
| NASA | National Aeronautics and Space Administration |
| RI | Remedial Investigation |
| SSFL | Santa Susana Field Laboratory |
| TCE | trichloroethene |
| VCAPCD | Ventura County Air Pollution Control District |
| VOC | volatile organic compounds |

# 1.0 INTRODUCTION

This work plan presents an approach for collecting field data that will aid in evaluating the effectiveness, implementability and cost of using vapor extraction as a technology for removing volatile organic compounds (VOCs) from the unsaturated bedrock of the Chatsworth formation that underlies the Santa Susana Field Laboratory (SSFL). Results from implementing the bedrock vapor extraction (BVE) field experiment will be used in the feasibility study (FS) that will be conducted for the SSFL. Vapor extraction is a well-established treatment technology for the remediation of VOCs[1] in contaminated soil (i.e., unlithified sediments), but its effectiveness, implementability and cost in fractured sedimentary bedrock settings like the Chatsworth formation are not well established.

The SSFL is located in the southeast corner of Ventura County, 29 miles northwest of downtown Los Angeles, California. The location of the SSFL and its surrounding vicinity is shown on Figure 1-1. The SSFL is jointly owned by The Boeing Company (Boeing) and the federal government (administered by the National Aeronautics and Space Administration [NASA]) and is operated by Boeing. The United States Department of Energy (DOE) used a portion of the SSFL. However, there are no longer active DOE operations and some facilities have been decommissioned and demolished. This work plan has been prepared by MWH on behalf of Boeing, NASA and DOE.

Previous environmental investigations have shown that the Chatsworth formation beneath portions of the SSFL has been impacted by releases of chemicals from historical operations, with trichloroethene (TCE) being the compound detected at the highest concentration and with the greatest frequency. BVE was selected for field testing in the unsaturated Chatsworth formation

[1] Vapor extraction is applicable when the contaminants present in the subsurface are volatile. As a simplified guideline, a compound or mixture of compounds are likely candidates for vapor extraction if their physical properties include: vapor pressures equivalent to or greater than 1.0 millimeter of mercury at 20°C; and Henry's law constants greater than 0.001 atm·m$^3$/mol, (or greater than 0.01 in the dimensionless form of Henry's law constant). VOCs such as TCE and its daughter products are examples of contaminants amenable to vapor extraction.

to assess its potential applicability as a technology that may achieve target remedial action objectives. The unsaturated portions of the Chatsworth formation are also referred to in this work plan as the bedrock vadose zone. Other remedial technologies have been identified for testing in the saturated portions of the Chatsworth formation as outlined in the FS work plan.

Section 2 of this work plan provides supporting background information including a set of performance criteria for the field experiment. Section 3 presents an evaluation of available sites for the field experiment, provides a rank order of available sites and describes the conditions at the site selected for the field experiment. Section 4 describes the extraction and monitoring well designs and layout for conducting the BVE field experiment at the selected site, and Section 5 provides a list of references.

# 2.0 BACKGROUND INFORMATION

This section of the work plan provides an overview of the current understanding of the conditions in the vadose zone bedrock related to the potential for mass removal of VOCs from this portion of the Chatsworth formation. A review of the Chatsworth formation is first provided, followed by a discussion of the contaminant conditions, VOC release and transport mechanisms, and the implications of these conditions relative to mass removal by applying pneumatic methods. Performance criteria for the BVE field experiment are also proposed.

## 2.1 CHATSWORTH FORMATION

The Chatsworth formation is a deep-sea turbidite formation composed primarily of sandstone with interbeds of siltstone and shale. It strikes N70$^{o}$E and dips about 25$^{o}$ to 30$^{o}$ to the northwest within the SSFL. A number of faults and deformation bands are present within and adjacent to the facility, nearly all of which dip steeply.

The Chatsworth formation is a dual-porosity system where the matrix porosity provided by interconnected pores is large (about 0.13), while the bulk fracture porosity is orders of magnitude smaller ($1x10^{-3}$ to $1x10^{-5}$). The composition of the rock matrix includes abundant reactive minerals and appreciable natural organic matter (0.21 percent for sandstones). Its fracture network is a systematic arrangement of bedding parallel fractures and steeply-dipping joints, with fracture network spacing and apertures spatially variable across the SSFL due to variability in lithology and structural characteristics.

## 2.2 VOC CHARACTERIZATION IN THE BEDROCK VADOSE ZONE

VOCs in the unsaturated portions of the Chatsworth formation have been characterized through the collection and analysis of rock core samples from coreholes that were positioned at or near locations across the SSFL where chlorinated solvents, primarily TCE, entered the subsurface. Sources in the bedrock that have been characterized using rock core analyses are shown in Figure 2-1. Characterization of VOCs in the vadose zone bedrock has primarily targeted five chlorinated ethenes that include: tetrachloroethene, TCE, cis- and trans- isomers of

1,2-dichloroethene (DCE), 1, 1-DCE; and chlorofluorocarbon (CFC)-113. A subset of samples (about 5 percent) was also analyzed for a full suite of compounds included in EPA analytical Method 8260.

Information contained in the following reports provide results regarding the occurrence and distribution of VOCs in the unsaturated zone:

*Evolution of TCE Source Zones and Plumes in the Chatsworth Formation Groundwater*, Santa Susana Field Laboratory, Parker and Cherry, 2000 (Appendix E in Montgomery Watson, 2000)

*Final Report, Source Zone Characterization at the Santa Susana Field Laboratory: Rock Core VOC Results for Core Holes C1 through C7* (Hurley et al, 2007a).

*Rock Core VOC Results for Corehole C8: Source Zone Characterization at the Santa Susana Field Laboratory Addendum Report No. 1* (Hurley et al, 2007b).

*Rock Core VOC Results for Corehole C9 (RD-84): Source Zone Characterization at the Santa Susana Field Laboratory Addendum Report No. 3* (Hurley et al, 2007c).

The latter three of these four reports contain cumulative mass plots of TCE, both in the unsaturated and saturated portions of the bedrock. The cumulative mass plots were reproduced for this work plan and are shown in Figure 2-2. The distribution of TCE in the unsaturated zone relative to that below the water table is summarized in Table 2-1. As can be seen in the figure and table, the relative mass contribution of TCE in the unsaturated zone to the total mass profile within the coreholes is highly variable and ranges from a low of 1 percent in corehole C-6 at the Delta Remedial Investigation (RI) site in Area II to 95 percent at corehole C-8 at the Former Sodium Disposal Facility (FSDF) RI site in Area IV. Various factors affect this distribution and include: the total completion depth of the corehole, the thickness of the vadose zone, the distance from the input location, the total mass released into the ground, and the penetration depth of immiscible phase TCE below the water table.

## 2.3 VOC RELEASE AND TRANSPORT MECHANISMS IN THE BEDROCK VADOSE ZONE

Throughout the history of operations at the SSFL, VOC transport within the bedrock vadose zone at the SSFL likely occurred in one or more of three different forms: gaseous-phase diffusion due to small releases at or just beneath the ground surface; dissolved-phase carried by recharge waters or seepage beneath ponds containing dissolved VOCs in the surface water; or as an immiscible-phase from large and/or persistent releases of primarily TCE. TCE dense non-aqueous phase liquid (DNAPL) releases would have initially flowed into the fracture network and spontaneously imbibed into the unsaturated bedrock matrix. TCE DNAPL penetration into the unsaturated rock matrix was restricted due to the relatively high vadose zone water content (i.e., ~70 percent on average). Equilibrium partitioning of the VOCs in the vadose zone bedrock has occurred, resulting in the exchange of mass between the vadose zone porewater, air, and sorption onto natural organic matter. Decades have passed since most releases of VOCs occurred. Currently, the vast majority of VOC mass is present in the rock matrix blocks of the vadose zone, with very little being present in the fracture network. VOC concentrations in the fracture network are in close equilibrium with concentrations present in the rock matrix near the fracture faces. Depending upon the transport mechanism and matrix block size, VOCs may be present throughout the unsaturated rock matrix or have penetrated into them a distance of a meter or more.

## 2.4 CONDITIONS CONTROLLING MASS REMOVAL/ TRANSFORMATION

The conditions in the unsaturated Chatsworth formation bedrock (i.e. bedrock vadose zone) beneath the SSFL have been documented in a number of reports in addition to those identified in Section 2.2. (Cherry, McWhorter and Parker, 2007; Hurley et al, 2007a, b, and c; Pierce, 2005; Montgomery Watson, 2000; MWH, 2008).

The movement of air or other fluids in the fracture network is believed to be generally well connected, both horizontally and vertically. However, it is expected that a few fracture zones within a vertical borehole will transmit most of the air or gas flowing across and/or within the hole.

The bulk intrinsic permeability of the Chatsworth formation is low to moderate, ranging from about $1x10^{-11}$ square centimeters ($cm^2$) to about $5x10^{-10}$ $cm^2$, with nearly all of the permeability being supplied by flow through the fracture network. The bulk intrinsic permeability is also spatially variable across the SSFL due to changes in the fracture network porosity.

The average air permeability in the rock matrix is very low, being about $5x10^{-13}$ $cm^2$ for sandstones (relative permeability of about 0.15) and a factor of 1,000 to 10,000 lower for siltstones/shales. The very low air permeability in the rock matrix is attributable to the low intrinsic permeability of the rock and to the small amount of space occupied by air in the rock matrix, which is estimated to be about 4 percent of the rock volume for sandstones, with the remaining percentages comprised of solids (87 percent) and water (9 percent). The relatively high water content in the rock matrix results from recharge that occurs at the SSFL - which is estimated to be about 6 percent of the mean annual precipitation or about 1 inch per year - and capillary forces in the rock matrix.

## 2.5 IMPLICATIONS OF VADOSE ZONE PNEUMATIC AND CONTAMINANT CONDITIONS ON VAPOR EXTRACTION FIELD EXPERIMENT DESIGN

The conditions described above are critical inputs to the performance objectives and design of the bedrock vapor extraction field experiment. Based on the characteristics described above, the following were given consideration in establishing the performance objectives and design:

- The flow of air or gases through the bedrock vadose zone will predominantly occur through the fracture network, which occupies a very small fraction of the bulk volume of the vadose zone ($1x10^{-3}$ to $1x10^{-5}$). This condition should allow for a large volume of rock to be influenced by an applied vacuum from a single vertical extraction well and yield relatively small flows.
- Vacuum responses will be fairly rapid and measurable at appreciable distances at monitoring locations intercepting discrete fractures. Such will be the case only when there is no appreciable vertical component of air flow from the ground surface to the extraction well. Alternately, vacuum responses at monitoring locations in the middle of rock matrix blocks will be slower under an applied vacuum.
- Geologic features that have been considered to either locally restrict (i.e. siltstones/ shales/ faults) or potentially enhance fluid flow (i.e. faults) are likely to appreciably affect the vacuum responses hypothesized above depending on their position relative to the extraction and monitoring points.

- Experience regarding advective flow paths in monitoring wells screened in the saturated zone (i.e. that most flow occurs within a few transmissive fracture zones in a vertical borehole) should be considered in the design of the extraction well. Consideration of this experience would indicate that a well with a longer open interval will have a higher probability of intercepting the more active fractures local to the well. This design consideration will have to be balanced against the proximity of the open interval to the ground surface to minimize potential vertical flow effects.
- The mass flow rate of VOCs in the extracted gas will be highest immediately after initiating extraction and will rapidly fall shortly after start-up as cleaner air is drawn in from the perimeter and ground surface. VOC mass removal efficiency from the rock matrix blocks is optimal under continuous operation of the blower because the VOC concentration gradients between the air moving in the fracture network and that in the rock matrix blocks is steep. These steeper concentration gradients enhance the rate of diffusion from the rock matrix blocks to the fractures. However, operational efficiency, defined here as the VOC mass flow rate per kilowatt-hour used, can be optimized by the episodic operation of the blower.

## 2.6 PERFORMANCE CRITERIA FOR THE BVE FIELD EXPERIMENT

The implications that the physical system of the bedrock vadose zone has on vapor extraction were used to establish performance criteria for the BVE field experiment and they are as follows:

1. Evaluate the production of air from an extraction well(s).
2. Evaluate the vacuum response in fractures and in matrix blocks.
3. Evaluate the effects of lithology changes and or structural features on the advective flow paths in the formation.
4. Evaluate the VOC mass flow rate over time.
5. Evaluate the diffusive response of VOCs from the rock matrix blocks post-treatment.

These performance criteria are used in developing the design and monitoring details for the BVE field experiment. Results from the field experiment will be used in discussing how these objectives were achieved such that the information can be considered in the FS in assessing the effectiveness, implementability and cost of this technology for the bedrock vadose zone at the SSFL.

# 3.0 SITE SELECTION AND CONDITIONS AT THE PROPOSED SITE

The 11 source zone coreholes where the occurrence and distribution of VOCs in the vadose zone bedrock has been characterized were each evaluated as candidates for the BVE field experiment. Locations are shown in Figure 2-1. The criteria considered in ranking and selecting a location for the field experiment were: the VOC mass and distribution in the vadose zone; site accessibility; vadose zone thickness; and general characterization information to support design of the field experiment. Considerations of the VOC mass in the vadose zone included both the total mass present in the unsaturated zone, its vertical distribution, and operational usage related to the projected VOC releases that may have occurred. The most favorable sites would include those with an appreciable mass and a fairly broad distribution in the vertical VOC characterization profile at a location of either documented or suspected large inputs. Vertical characterization profiles for TCE from the 11 source zone characterization rock core profiles have been reproduced from previous reports and are included in this work plan in Appendix A. Other VOCs that have been identified and quantified are also shown on the plots as appropriate.

Based on this first criterion, five locations were screened out as candidates for the field experiment and included coreholes: RD-35B at the Instrument and Equipment Laboratory (IEL) RI site; C-2 at the Canyon RI site; C-5 at the Alfa RI site; C-7 at the Expendable Launch Vehicle RI site; and C-9 (now identified as well RD-84) at the B-1 RI site. Each of these locations contained less than 3 grams per square meter ($g/m^2$) as an equivalent TCE mass[2], as shown in Table 2-1.

Of the remaining 6 locations, the area near corehole C-3 at the Components Test Laboratory (CTL)-I RI site is physically constrained such that installation of the proper instrumentation for a field experiment would not be practicable. Also, the area within corehole C-6 at the Delta RI site has a relatively thin bedrock vadose zone (less than 40 feet) and the distribution of VOCs in the

[2] The units of mass (M) per length squared ($L^2$) result from multiplying: (the sum of the measured concentrations of TCE and its daughter products (on a molar basis) from each sample (units of $M/L^3$)) by (the length of the sample interval (units of L), defined as the distance between the midpoint between the sample above and the sample below).

vertical profile lies within a narrow band near an area of locally-perched groundwater as can be seen in the vertical profile provided in Appendix A.

The four remaining locations were given further consideration as the location for the BVE field experiment and included coreholes: C-1 at the IEL RFI site; C-4 at the Bowl RI site; C-8 at the FSDF RI site and RD-46B at the CTL-III RI site. The location in the vicinity of corehole C-1 at the IEL RFI site was screened out, as this area is proposed for a groundwater chemical oxidation field experiment and there are logistical concerns associated with interference between two different test activities. Of the 3 remaining source locations for the BVE field experiment, the following order of preference resulted:

1. Corehole C-4 at the Bowl RI site,
2. Corehole C-8 at the FSDF RI site, and
3. The corehole that was subsequently converted to monitoring well RD-46B at the CTL-III RI site.

The area in the vicinity of corehole C-4 at the Bowl RI site was selected as the first priority site for the BVE field experiment for the following:

- The thickness of the vadose zone is about 90 feet and there are appreciable detections of TCE and its daughter products throughout the vertical profile in the vadose zone,
- The area is readily accessible for the placement of equipment and test infrastructure,
- The area is well characterized as to the geologic framework and the effects, if any, of different geologic features on BVE system design and performance can be evaluated, and
- The Bowl RI site has been previously reported to be a location where a considerable mass of TCE entered the subsurface (CH2MHill, 1993).

The area near corehole C-8 at the FSDF RI site was identified as a second priority field site for the BVE test because it has 3 of the 4 same characteristics as the area near corehole C-4 at the Bowl RI site. However, the FSDF RI site is expected to have an appreciably lower bulk air permeability than the Bowl RI site based on observations of fracture spacing and fault occurrence in ground exposures made during excavations at the FSDF for interim measures and the results of hydraulic tests in the saturated zone. It is also worth mentioning that the area above corehole C-8 has had an engineered cap constructed of native fill placed over the

backfilled excavation that could serve as a lower permeability feature to evaluate the flow of air from the ground surface.

The area near the corehole that was subsequently converted to monitoring well RD-46B at the CTL-III RI site was identified as a third priority field site for the BVE test because it also has similar characteristics to the other two sites referenced above. The primary difference with this location is that the vertical profile of rock core results in the vadose zone is appreciably less frequent than the subsequent coreholes, as this was the first location drilled at the SSFL to characterize VOCs in rock pore water.

## 3.1 CONDITIONS AT THE SELECTED TEST LOCATION

Corehole C-4, which characterizes the bedrock vadose zone at the Bowl RI site, is located on the leading edge of the former Bowl skim pond, at the end of the Bowl spillway. Site features are shown in Figure 3-1. The shallow slope of the Bowl spillway would have likely affected the flow, pooling, and evaporation of any TCE released subsequent to its use in the cleaning of rocket engine components. The corehole is located at the toe of spillways from two of the three test stands, close to the former skim pond. The skim pond contained wastewater from testing operations during the years that the Bowl area was active (Hurley et al, 2007a).

At corehole C-4 in the Bowl RI site, a thin layer of unconsolidated silty sand is found from beneath the asphaltic concrete (AC) surface to 3 feet below ground surface (bgs). Bedrock is encountered below a depth of 3 feet to the total depth of the hole. In the vicinity of C-4, the bedrock in the upper 40 feet has been characterized as weathered based on the installation of piezometers (PZ-85A/B) that have been designed to monitor the potential for the shallow ponding of groundwater that may occur seasonally. Lithologically, the bedrock in the vadose zone is described as primarily sandstone with a sequence of interbedded mudstones, siltstones and shales between a depth of about 60 to 80 feet bgs.

Stratigraphically, corehole C-4 is positioned in the Bowl member, which is the lowest stratigraphic member of the Upper Chatsworth formation. The Bowl member consists of primarily coarse- to medium-grained arkosic sandstone that locally contains thin conglomerate

beds and contains a significant number of thin, finer-grained beds. Two of these beds, named the Upper and Lower Bowl beds, are mappable in the field and can also be identified in drilling and geophysical logs (MWH, 2002). Corehole C-4 starts in the sandstones of the Bowl member and penetrates through the Upper and Lower Bowl beds and into the Lower Chatsworth formation at depth. A cross-section depicting the staratigraphy at corehole C-4 and two Chatsworth formation monitoring wells located to the southeast is shown in Figure 3-2. The vadose zone at this location extends through the Upper Bowl bed from approximately 60 to 80 feet bgs, to a short distance below the base of this bed.

A structural feature identified as the Bowl structure (see Figure 3-1) has been interpreted to lie within the area characterized by corehole C-4 (MWH, 2007). Structural features have been defined for the SSFL as features where outcrops are insufficient to assess the magnitude of off-set in the stratigraphy created by the structural feature. The existence of the Bowl structure is inferred from an aerial photo lineament expressed as a topographic low and the presence of a deformation band exposed in outcrop that strikes parallel to the aerial photo lineament. The aerial photo lineament ends where it intersects colluvium west of RD-2. The Bowl structure has been tentatively interpreted to extend westward to another fault at the SSFL referred to as the Shear Zone.

Groundwater in the bedrock is first encountered at a depth of about 90 feet bgs at corehole C-4. A shallow zone of perched groundwater has also periodically been measured at depths between 10 and 20 feet bgs. However, its occurrence is seasonal and related to appreciable rain events (MWH, 2003). It should be noted that corehole C-4 was retrofitted with a blank FLUTe liner to seal the hole shortly after it was drilled to reduce the potential vertical flow of groundwater within the corehole. This blank liner remains in place as of the date of this work plan.

The existence of chlorinated VOCs in C-4 and within the subsurface in general at the Bowl RI site is primarily due to the use of TCE for the cleaning of rocket engine components. The site was used for liquid-propellant rocket engine testing activities and was in operation from 1949 to the early 1960s. Engine testing occurred at three test stands at the site, and primarily used

petroleum-based compounds as the "fuel" and liquid oxygen as the "oxidizer". Solvents, primarily TCE, were used for cleaning of engine components (MWH, 2004).

Chlorinated ethene concentrations were detected throughout the entire bedrock vadose zone at C-4, which extends vertically through approximately 90 feet as shown in Figure 3-3. TCE was the most prevalent of the chlorinated ethenes, with significant levels of cis-1,2-DCE and 1,1-DCE also detected within the bedrock vadose zone. The maximum TCE concentration detected in the rock core from this corehole was 55 mg/L (in units of equivalent porewater concentration, at 67 feet bgs within the Upper Bowl bed). The full list of Environmental Protection Agency (EPA) Method 8260 target analytes was also characterized in rock core collected from this corehole by analyzing 5 percent of the total samples collected. There were no other noteworthy detections of other VOCs in the vadose zone from this corehole as a result of these analyses.

# 4.0 EXTRACTION WELL AND MONITORING SYSTEM DESIGN

Performance objectives for the BVE field experiment were described in Section 2.6 and included:

1. Evaluate the production of air from an extraction well(s).
2. Evaluate the vacuum response in fractures and in matrix blocks.
3. Evaluate the effects of lithology changes and or structural features on the advective flow paths in the formation.
4. Evaluate the VOC mass flow rate over time.
5. Evaluate the diffusive response of VOCs from the rock matrix blocks post-treatment.

These performance objectives were addressed in the design of the BVE pilot test as summarized in Table 4-1. This table lists the performance objectives; the data that are needed to assess performance for each objective; the method to be used to collect those data; the location(s) from which the data will be collected; and the frequencies of data collection.

Design elements developed to date include a conceptual plan view layout of the BVE well and monitoring probes (Figure 4-1), one generalized cross-section showing the same in vertical profile (Figure 4-2) and conceptual completion diagrams for both the BVE well and monitoring probes (Figure 4-3).

The BVE well location is shown in plan view in Figure 4-1. The BVE well was positioned near corehole C-4 to ensure that it is located within the same VOC source area and to make maximum use of the existing C-4 rock core analytical results. The location was also selected to be along strike and slightly updip from corehole C-4 to allow for the installation of an extraction well screen above the projected water table and below the base of the Upper Bowl bed. The conceptual BVE well completion is shown in vertical profile in Figures 4-2 and 4-3. The extraction well was designed with separate extraction casings in four discrete vertical zones in a single large-diameter borehole. The two shallowest screened intervals were designed to intercept the sandstone that lies above the finer-grained Upper Bowl bed. Two discretely-screened

sections were chosen to allow for an evaluation to be made as to the degree of vertical air flow from the ground surface to the extraction well and to evaluate lithologic effects on the flow system. The third-deepest screened interval targets vapor extraction from the finer-grained Upper Bowl bed. The deepest screened interval is intended to intercept the sandstone that lies beneath the Upper Bowl bed. The discretely-screened intervals are separated by 5-foot thick seals to prevent the short-circuiting of air flow within the well bore. The extraction well casings will be manifolded together above ground to provide the flexibility to extract air from one or any combination of the four extraction zones. Actual installation details regarding screen positions and lengths for the BVE well will be based on rock core observations and geophysical logging data as indicated in Table 4-1. In particular, whereas the conceptual design in Figure 4-2 shows all of the BVE casings screened within the major lithologic members, some BVE well casings may be installed so as to span the contacts between these lithologic members if field data suggest that bedding plane partings exist at these contacts and may provide preferential flow paths. It is also worthy to note that the vadose zone within existing corehole C-4 will have to be sealed during the operation of the BVE field experiment and that there are methods available to accomplish this without abandoning the corehole (e.g. blank synthetic liners).

Similarly, each BVE monitoring well will be completed as a multilevel system of monitoring probes within discrete vertical intervals of a single borehole. Ten monitoring well locations are shown in the conceptual plan view in Figure 4-1 and vertical completions are conceptually shown on Figures 4-2 and 4-3. Most of the monitoring wells will be completed with three to four discrete vertical monitoring intervals. At least two BVE monitoring wells will be completed with a larger number of intervals (between six and ten) to provide additional vertical resolution, and to address, in particular, performance objective 2 by allowing the completion of some monitoring intervals in unfractured zones without sacrificing the ability to monitor fractured zones where most of the flow is expected to occur. The final design of the multilevel BVE monitoring wells will be based on the drilling and geophysical data to be collected during and following installation of the boreholes as indicated in Table 4-1. As with the BVE well casings, although Figure 4-2 conceptually shows all of the vadose zone monitoring intervals completed within the major lithologic units, some of the monitoring intervals may be installed so as to span

the contacts between these lithologic members if field data suggest that bedding plane partings exist at these contacts and may provide preferential flow paths.

The installation of multilevel vadose zone monitoring wells will be phased to allow the collection of preliminary data that will be used to further refine the numbers and locations of vadose zone monitoring wells, and to evaluate whether the installation of additional BVE wells may be desirable. Two to three of the multilevel vadose zone monitoring wells will initially be installed along with the BVE well. Alternatively, one or two of these monitoring wells may instead be completed as multilevel BVE wells that would also serve as monitoring points. Five existing shallow piezometers also lie within the general area of the proposed test location (PZ-84, -85A/B and -87A/B). Four of the piezometers are composed of two vertically-paired sets (PZ-85A/B and PZ-87A/B). All five piezometer locations will be modified to allow for the measurement of vacuum responses during the BVE test thereby providing additional spatial coverage to assess the flow of air in the subsurface.

A temporary vapor extraction and treatment system will be used to perform limited testing using this initial set of wells and existing piezometers. This preliminary BVE testing will focus primarily on evaluating vacuum response and distribution induced by a range of three to five blower vacuum and flow settings. These preliminary data will be used to optimize the number, types and locations of additional vadose zone monitoring and/or BVEwells, and to aid in the selection of the final extraction blower and associated treatment equipment.

The asphalt cover will be removed from the test area to eliminate whatever influence it might have on subsurface flow and vacuum conditions during the test. If test results suggest that the vertical flow of air from the ground surface to the extraction well may have reduced the distribution of vacuum responses (in particular when extracting from the shallowest extraction zone), additional tests may be performed with a temporary cover constructed of plastic sheeting and sandbags over the test area for comparison with the test results obtained without cover.

Before BVE testing begins, VOC concentrations at the multilevel vadose zone monitoring wells will be measured with a field PID to provide baseline conditions. Air samples will be collected from a portion of the monitoring wells for laboratory VOC analysis during this baseline

monitoring event to help calibrate the field PID measurements and to provide information about the types and ratios of VOCs present. A portion of these samples well also be analyzed for atmospheric gases, the results of which will be compared to the results from samples collected later during the testing to help evaluate the degree of vertical air flow from the ground surface. The locations, numbers and frequencies of air samples collected for laboratory VOC or atmospheric gases analyses during the BVE testing (Table 4-1) will be determined in the field based on field PID readings and observed trends in those readings. Further discussion of the reasoning behind the conceptual well layout presented in Figure 4-1 is presented below.

## 4.1 Discussion of Conceptual Well Layout

The conceptual well layout presented in Figure 4-1 was designed to satisfy multiple objectives. One multilevel vadose zone monitoring well array (Array 1) includes 3 wells aligned approximately along the strike of the Bowl Structure (roughly the direction defined by the line between well RD-2 and corehole C-4) as shown in Figure 4-1. The BVE well and the nearest three vadose zone monitoring wells of this array are also shown in cross-section in Figure 4-2. This monitoring array was designed to facilitate the evaluation of:

- Flow and vacuum in and across the Upper Bowl bed when extracting from above or below,
- Flow and vacuum in the sandstone members above and below the Upper Bowl bed (referred to as Bowl Members A and B) when extracting from within the Upper Bowl bed, and
- Vacuum distribution along strike of the Bowl structure.

A second vadose zone monitoring well array (Array 2) consists of six multilevel monitoring wells aligned approximately down dip to local bedding measurements (Figure 4-1). This array was designed to facilitate the evaluation of:

- Flow and vacuum within the four extraction zones and responses in adjacent zones for comparison with Array 1,
- Vacuum distribution down dip for comparison with the structure-parallel distribution, and
- The possible influence of a fault on vacuum distribution (the Bowl Structure traverses between the BVE well and two of the multilevel vadose zone monitoring wells).

One vadose zone monitoring well has also been positioned about 220 feet from and on the same side of the Bowl structure as the extraction well to assess the potential for distant vacuum responses.

As mentioned previously, the actual numbers, positions and construction details of BVE wells and multilevel BVE monitoring wells will be determined based on the field data collected from each borehole (Table 4-1), and on the preliminary BVE testing to be performed after the first phase of well installations is completed. All final well designs and locations will be developed with and approved by DTSC prior to installation.

## 4.2 Operations

The operation of the BVE field experiment will be conducted in two phases. The first phase will include the installation of the BVE well and two of the vadose zone monitoring wells. The vacuum/flow/response conditions will be evaluated during a series of short tests that are projected to occur over a period of 2 to 5 work days, depending upon field results. The data produced from this first phase of testing will be reduced and evaluated in consultation with DTSC. The second phase will include the installation of the additional vadose zone monitoring wells and/or additional BVE wells. The duration of the extraction phase of the BVE field experiment will be determined using the results from the first phase of testing along with calculations and/or models that may be used to project either or both pneumatic conditions and VOC mass flow rates during extraction and the recovery of VOC concentrations post-extraction. The duration of the second phase of testing will be developed in consultation with DTSC.

## 4.3 Permitting

Preliminary discussions with the Ventura County Air Pollution Control District (VCAPCD) have indicated that an Authority to Construct and Permit to Operate will be required to control VOC emissions discharging from the extraction system blower during the BVE field experiment. The VCAPCD offers a variance for short-term testing operations (less than 24 hours) that may be applicable to the first phase of preliminary testing. There is also a “flexible” Authority to Construct and Permit to Operate that allows a range of blower and equipment sizes to be

specified in the permit. This flexible permit may allow for the preliminary and longer-term BVE experiment equipment to be incorporated in a single permit. The permit requires the completion of a health risk assessment using the HARP model. This model can be completed and submitted by the permittee or by VCAPCD staff. The specific requirements and applicability of the short-term variance and the flexible Authority to Construct and Permit to Operate will be further investigated with the VCAPCD to determine the most effective approach to satisfying the BVE field experiment air permitting requirements.

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# TABLES

**Table 2-1**
**Summary of TCE Distribution in Unsaturated Zone at SSFL Coreholes**

| Corehole | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C-8 | C-9 |
|---|---|---|---|---|---|---|---|---|---|
| Mass in Unsaturated Bedrock ($g/m^2$) | 20 | 1.5 | 21 | 31 | 2 | 50 | 2 | 19 | 2.9 |
| Total Mass ($g/m^2$) | 100 | 10 | 30 | 90 | 5 | 4000 | 30 | 20 | 4 |
| % in Unsaturated Bedrock | 20% | 15% | 70% | 34% | 40% | 1% | 7% | 95% | 73% |

$g/m^2$ = grams per square meter

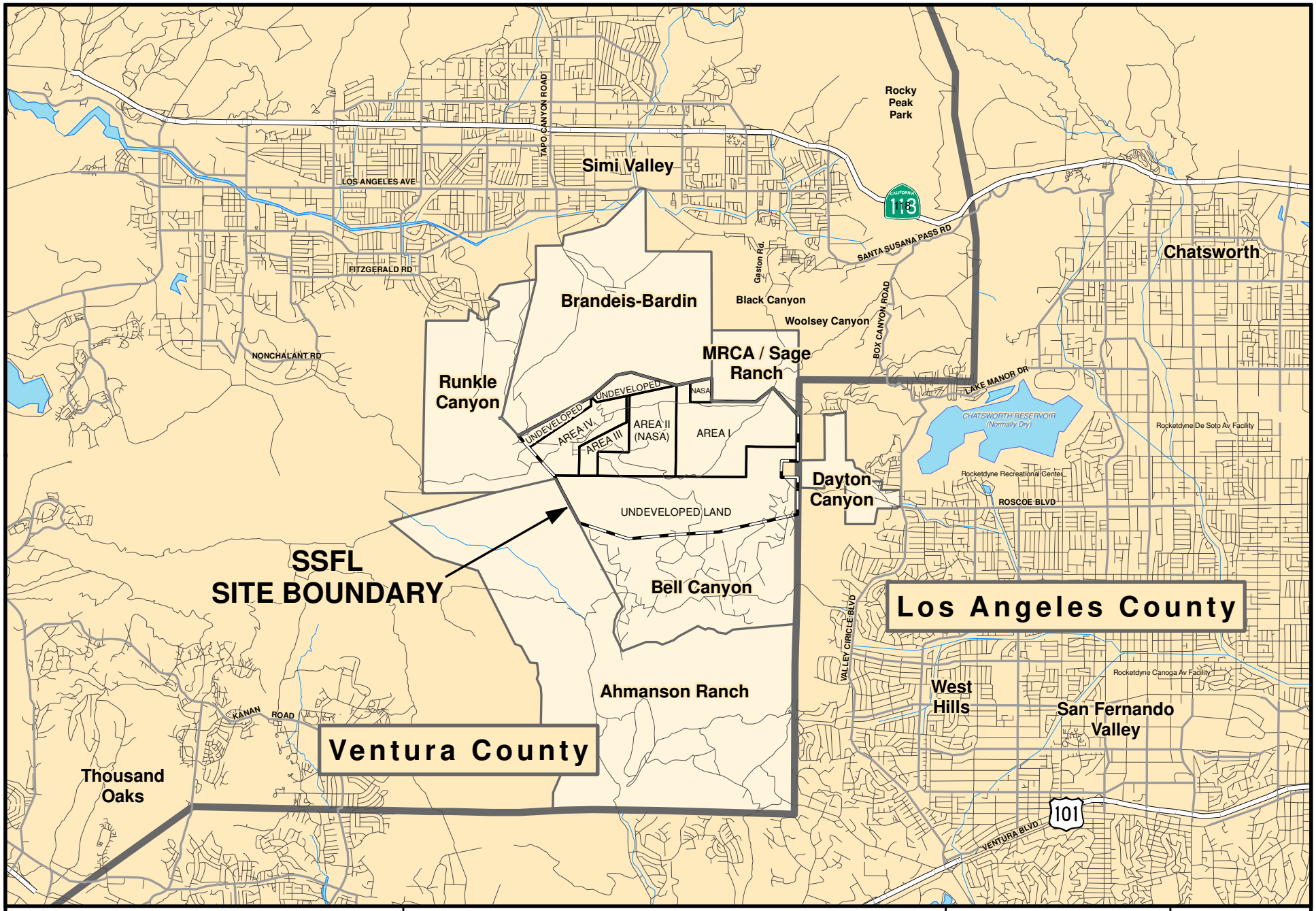
Table 4-1
Plan Overview, Bedrock Vapor Extraction Field Experiment
Santa Susana Field Laboratory

| Objective | Measurement or Parameter | Method | Location | Frequency |
|---|---|---|---|---|
| 1. Evaluate production of air from extraction well | Flow, vacuum, lithology, and fractures | • Monitor/record flow and vacuum<br>• Lithology via rock core, and natural gamma, density, and induction resistivity logging<br>• Fractures via rock core and optical televiewer (OTV) logging | Multilevel (ML) bedrock vapor extraction (BVE) well casings | Flow/vacuum at 3 to 5 blower settings for each BVE well casing |
| 2. Evaluate the vacuum response in the vadose zone in fractures and in matrix blocks | Time, vacuum, lithology, and fractures | • Monitor/record vacuum over time<br>• Lithology via drilling log, and natural gamma, density, and induction resistivity geophysical logging<br>• Fractures via OTV logging | ML BVE monitor wells (with intervals completed in fractured and unfractured zones) | Flow/vacuum at startup and every 5 minutes initially, decreasing in frequency as vacuum stabilizes |
| 3. Evaluate the effects of lithology and or structural features on the advective flow paths in the formation | Flow, vacuum, time, lithology, fractures, structural features, and concentrations of atmospheric gases | • Monitor/record flow and vacuum over time<br>• Lithology via drilling/core logs, and natural gamma, density, and induction resistivity geophysical logging<br>• Fractures via OTV logging<br>• Structural features via geologic mapping, drilling/core logs, and geophysical logs<br>• Vertical flow component from ground surface via atmospheric gases analysis | • Flow at ML BVE well casings<br>• Vacuum, lithology, fractures, structural features, atmospheric gases at ML BVE well casings and ML BVE monitor wells<br>• Vacuum, lithology, atmospheric gases at existing piezometers | • Flow/vacuum at startup and every 5 minutes initially, decreasing in frequency as vacuum stabilizes<br>• Atmospheric gases initially and at 2 to 3 additional times based on PID readings |
| 4. Evaluate the VOC mass flow rate over time | Flow, VOC concentration, time and lithology | • Monitor/record flow rate<br>• Monitor/record VOC concentrations over time with field PID and laboratory analysis of air samples<br>• Lithology via rock core, and natural gamma, density, and induction resistivity logging | ML BVE well casings | • Flow at startup and at time of each VOC monitoring/sampling<br>• VOC concentrations with PID at startup and every 2 minutes initially, decreasing in frequency based on observed rate of change<br>• Collect air samples for laboratory VOC analysis at startup and at 2 to 3 additional times based on PID readings |

Table 4-1
Plan Overview, Bedrock Vapor Extraction Field Experiment
Santa Susana Field Laboratory

| Objective | Measurement or Parameter | Method | Location | Frequency |
|---|---|---|---|---|
| 5. Evaluate the diffusive response of VOCs from the rock matrix blocks post-treatment | VOC concentration, time, lithology, and fractures | • Monitor/record VOC concentrations via field PID and laboratory analysis of air samples<br>• Lithology via drilling log, and natural gamma, density, and induction resistivity geophysical logging<br>• Fractures via OTV logging | ML BVE monitor wells | • PID readings upon blower shutdown and twice per day initially, decreasing in frequency based on observed rate of change<br>• Collect air samples for laboratory VOC analysis upon blower shutdown and at 2 to 3 additional times based on PID readings |

# FIGURES




1 inch = 1.5 miles

0 1.5 3 Miles

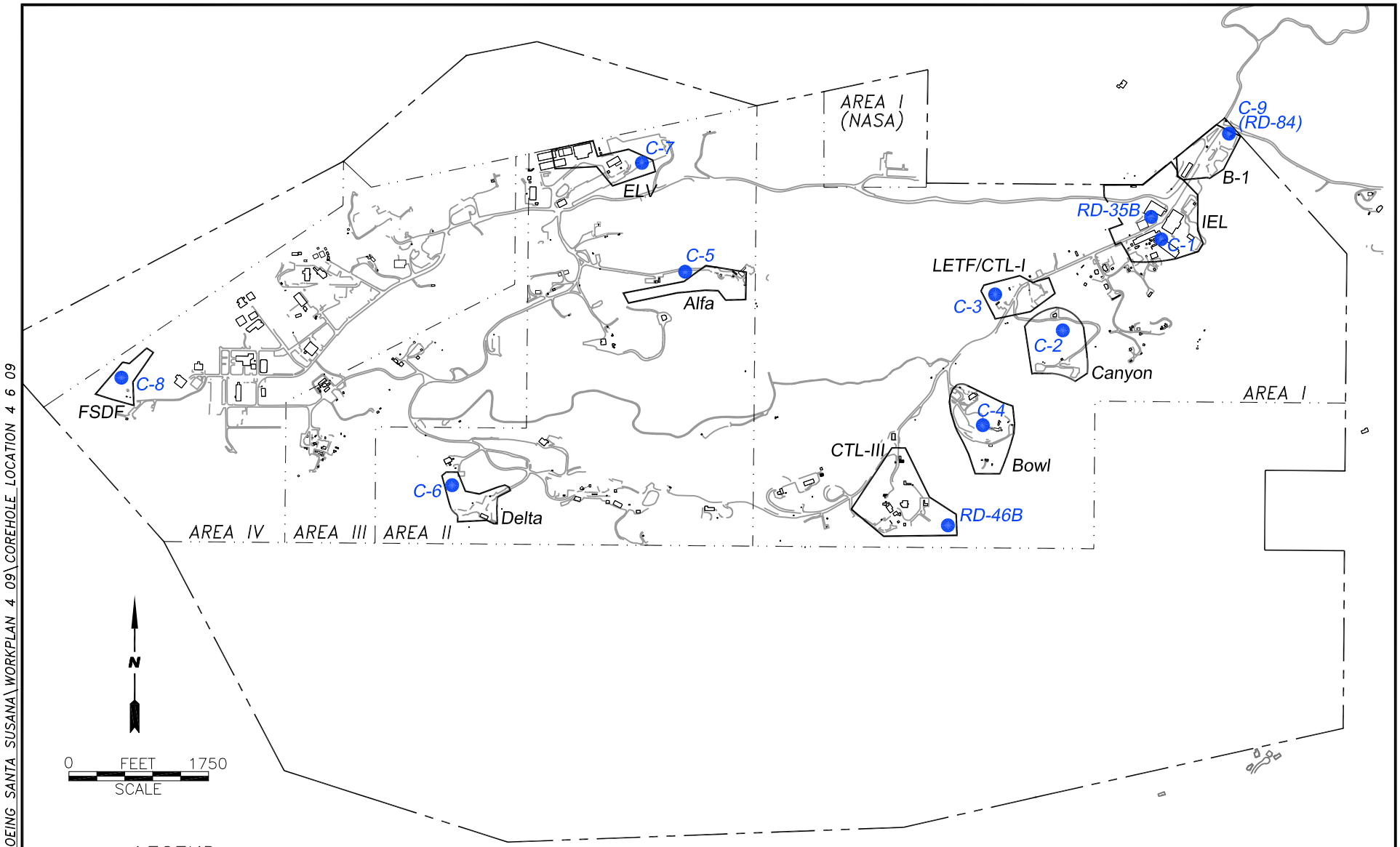
# SANTA SUSANA FIELD LABORATORY

Document: RFI-Report-Group1A-Bundle-Regional_Map.mxd

Date: Feb 04, 2009

## Regional Map

## FIGURE 1-1




FILE No. CAD_MLUEBKE\BOEING SANTA SUSANA\WORKPLAN 4 09\COREHOLE_LOCATION 4 6 09

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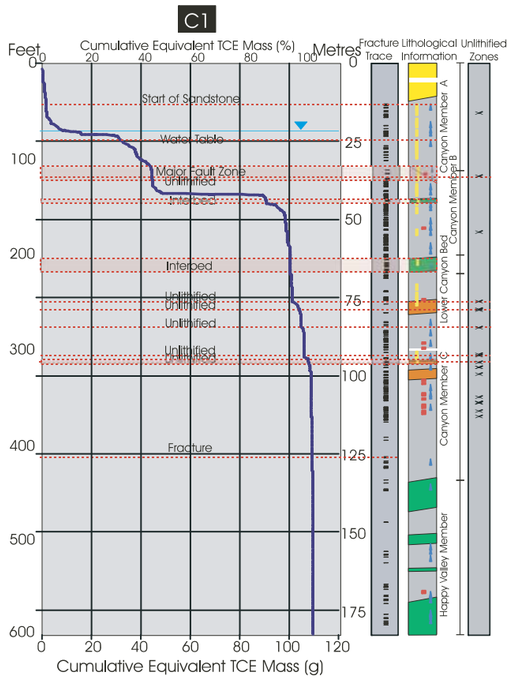
SANTA SUSANA FIELD LABORATORY
VENTURA COUNTY, CALIFORNIA
APRIL 2009

SOURCES CHARACTERIZED BY ROCK CORE ANALYSES

FIGURE 2-1



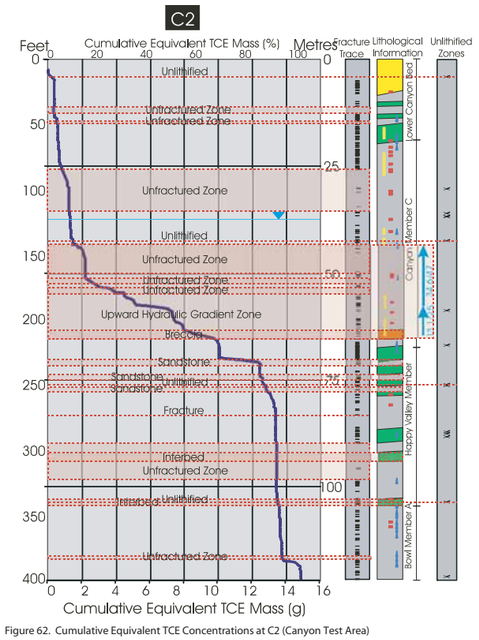




Figure 62. Cumulative Equivalent TCE Concentrations at C2 (Canyon Test Area)

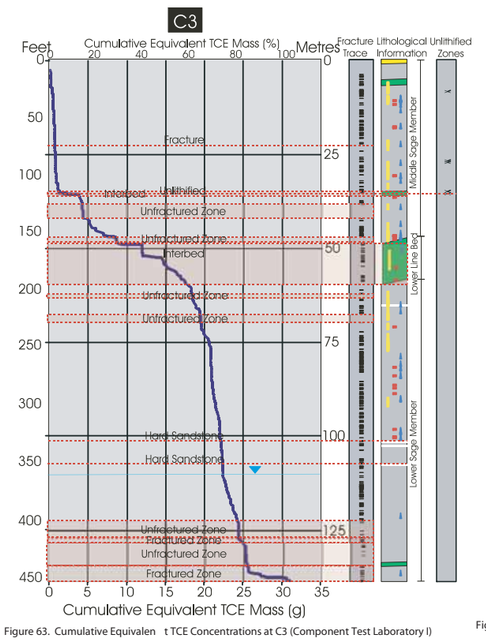



Figure 63. Cumulative Equivalen t TCE Concentrations at C3 (Component Test Laboratory I)

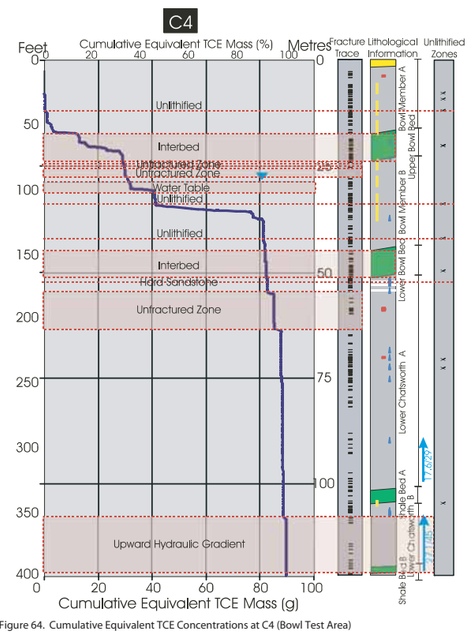



Figure 64. Cumulative Equivalent TCE Concentrations at C4 (Bowl Test Area)

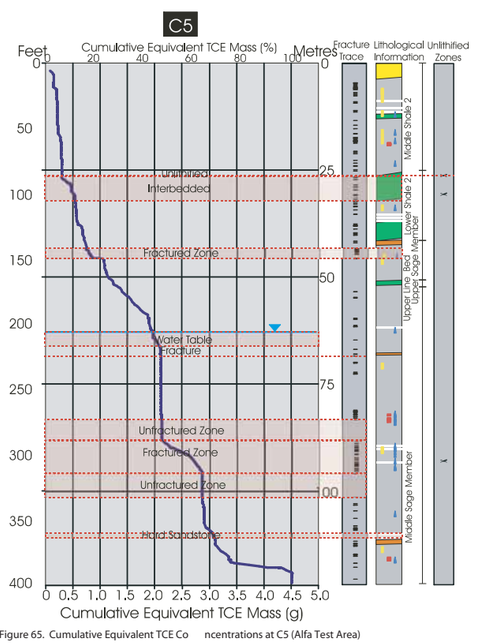



Figure 65. Cumulative Equivalent TCE Co ncentrations at C5 (Alfa Test Area)

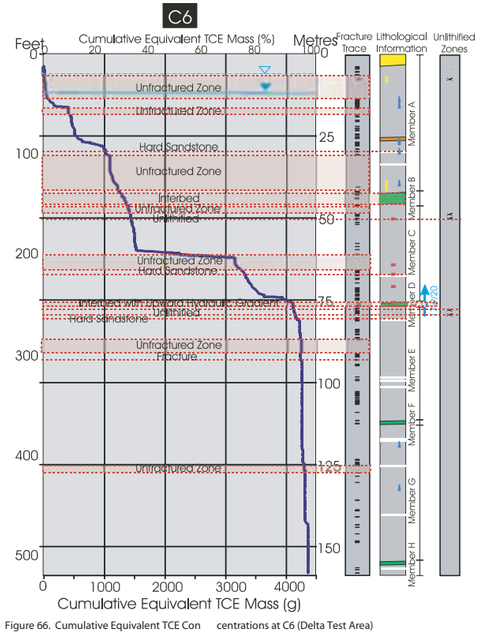



Figure 66. Cumulative Equivalent TCE Con centrations at C6 (Delta Test Area)

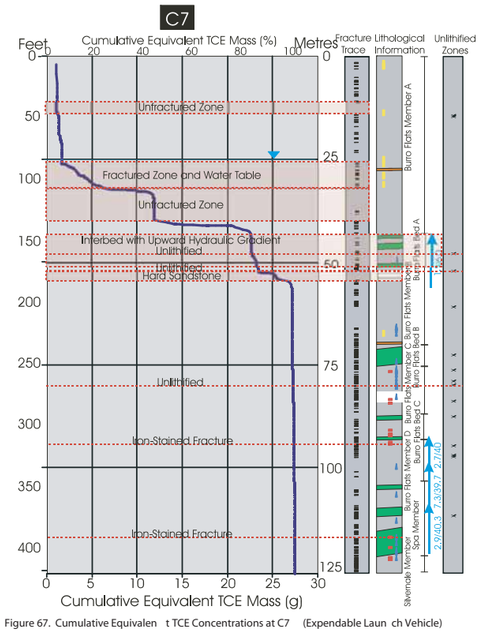



Figure 67. Cumulative Equivalen t TCE Concentrations at C7 (Expendable Laun ch Vehicle)

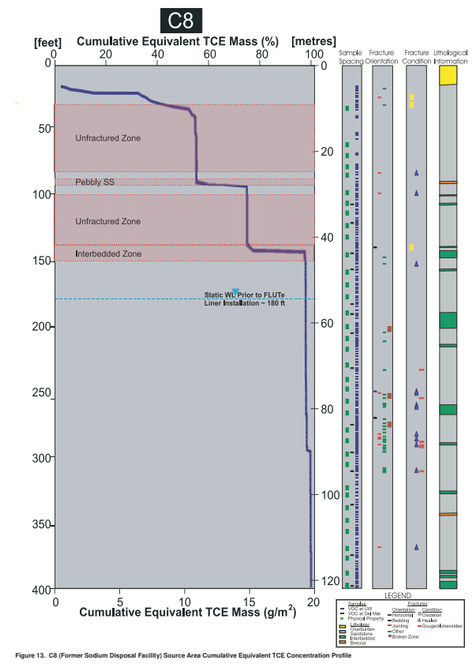



Figure 13. C8 (Former Sodium Disposal Facility) Source Area Cumulative Equivalent TCE Concentration Profile

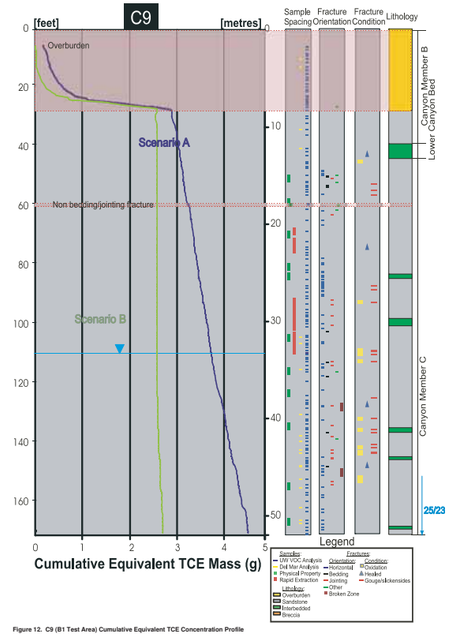



Figure 12. C9 (B1 Test Area) Cumulative Equivalent TCE Concentration Profile

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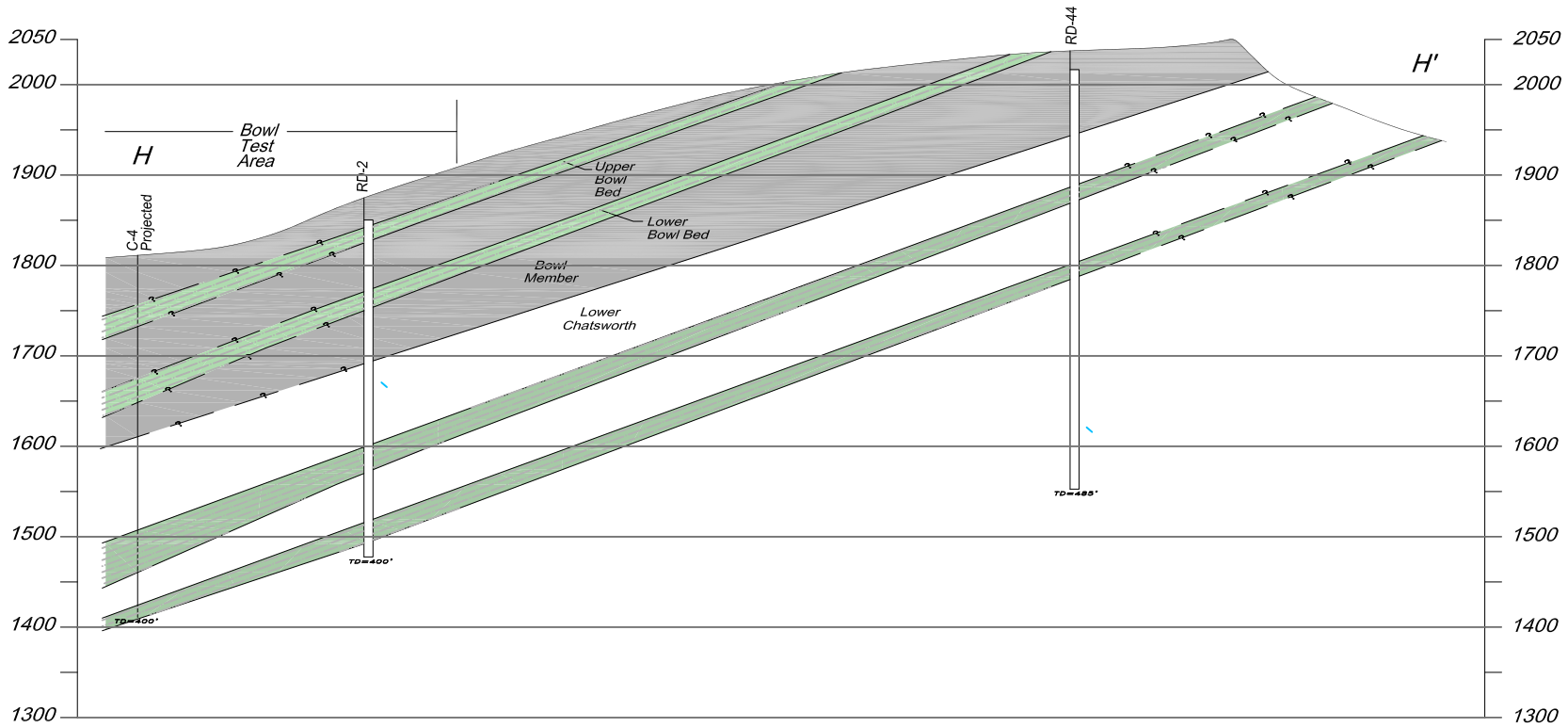
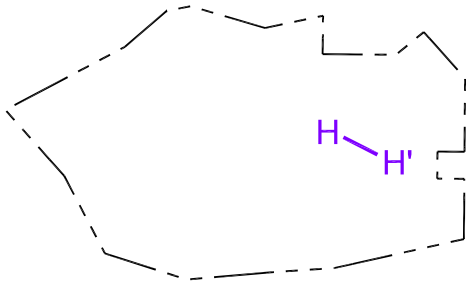
Santa Susana Field Laboratory
Ventura County, CA
April 2009
FIGURE 2-2
Cumulative Equivalent TCE Mass
Profiles Coreholes C-1 through C-9

Please Note: The original version of this figure includes colorized features and shading. A black and white copy of this figure should not be used because it may not accurately represent the information presented.
Shear Zone Located ~300' Northwest
PZ087A/B
PZ084
PZ085A/B
C-4
RD-2
RD-44 Located ~700' Southeast
Bowl Structure
1820
1840
1860
1880
1920
1810
34
26
24
36
Legend
Chatsworth Formation Groundwater Monitoring Well
Corehole Location
Near-Surface Groundwater Piezometer
Strike and Dip of Bedding
Structure Location
N
0 FEET 75
SCALE
MWH
SANTA SUSANA FIELD LABORATORY
VENTURA COUNTY, CALIFORNIA
APRIL 2009
BOWL SITE PLAN
FIGURE 3-1
FILE No. CAD MLUEBKE\BOEING SANTA SUSANA\WORKPLAN FS 4 09\BOWL RFI SITE PLAN 4 6 09




Cross-Section Location

0 FEET 200
SCALE

*Please Note: The original version of this figure includes colorized features and shading. A black and white copy of this figure should not be used because it may not accurately represent the information presented.*

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*VENTURA COUNTY, CALIFORNIA*
*APRIL 2009*

CROSS-SECTION DEPICTING CHATSWORTH FORMATION STRATIGRAPHY BOWL SITE

*FIGURE 3-2*

*FILE No. CAD MLUEBKE\BOEING SANTA SUSANA\WORKPLAN 4 09\CHATSWORTH SECTION*

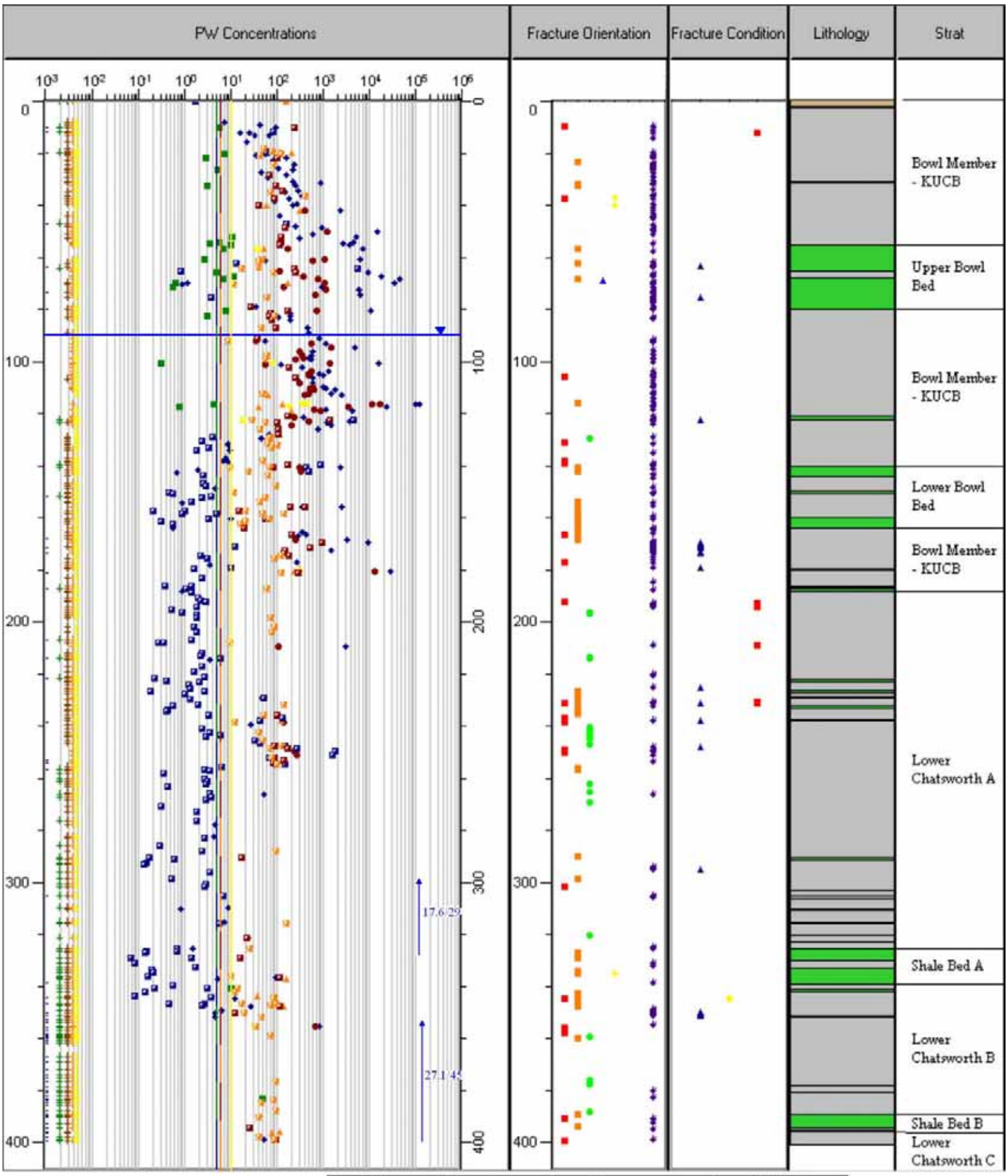
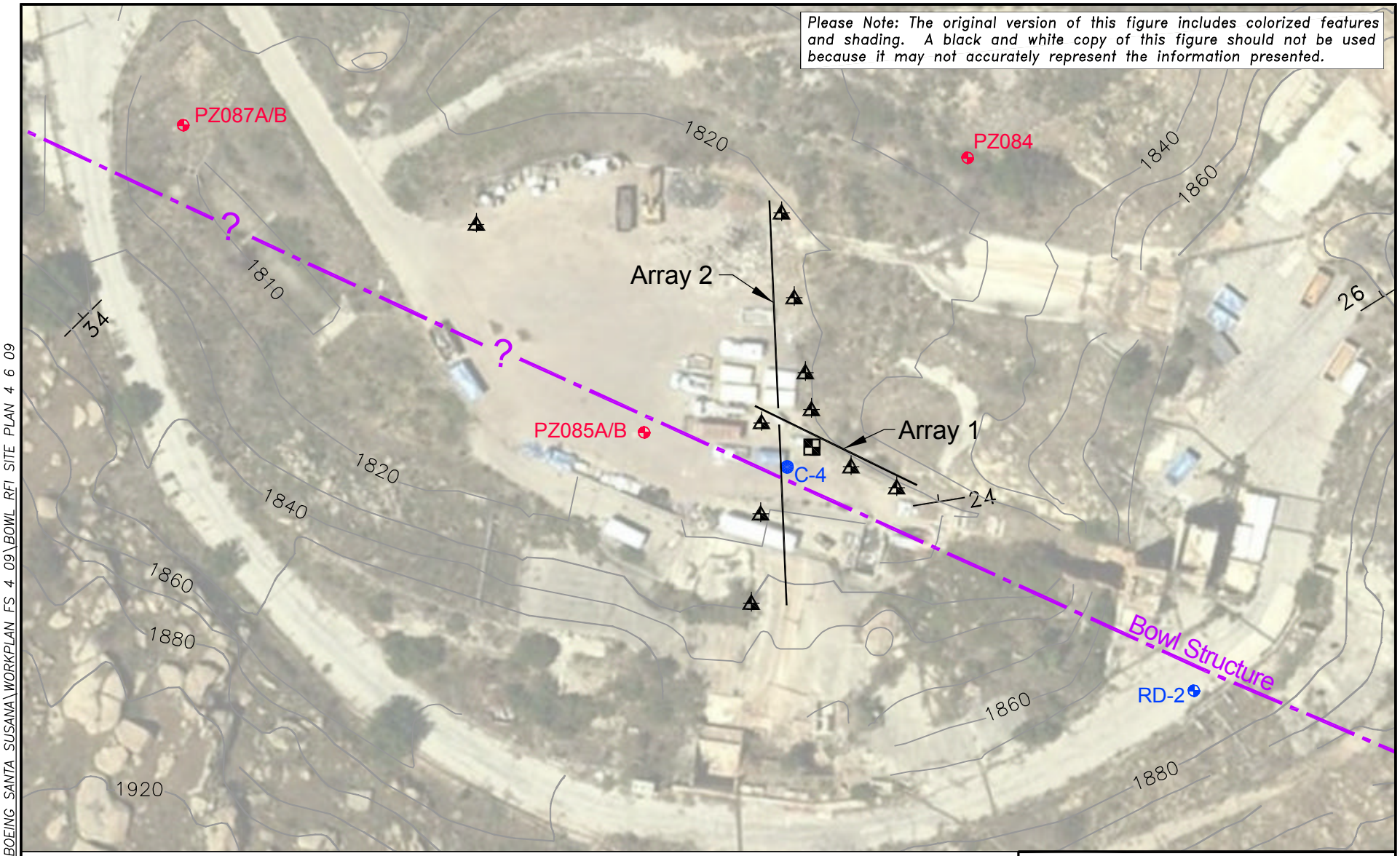



**Figure 3-3 C-4 Concentration Profile of Chlorinated Ethenes in Rock**

Figure 48 from Final Report, Source Zone Characterization at the Santa Susana Field Laboratory: Rock Core VOC Results for Core Holes C1 through C7. Hurley, et al, 2007.




FILE No. CAD MLUEBKE\BOEING SANTA SUSANA\WORKPLAN FS 4 09\BOWL RFI SITE PLAN 4 6 09

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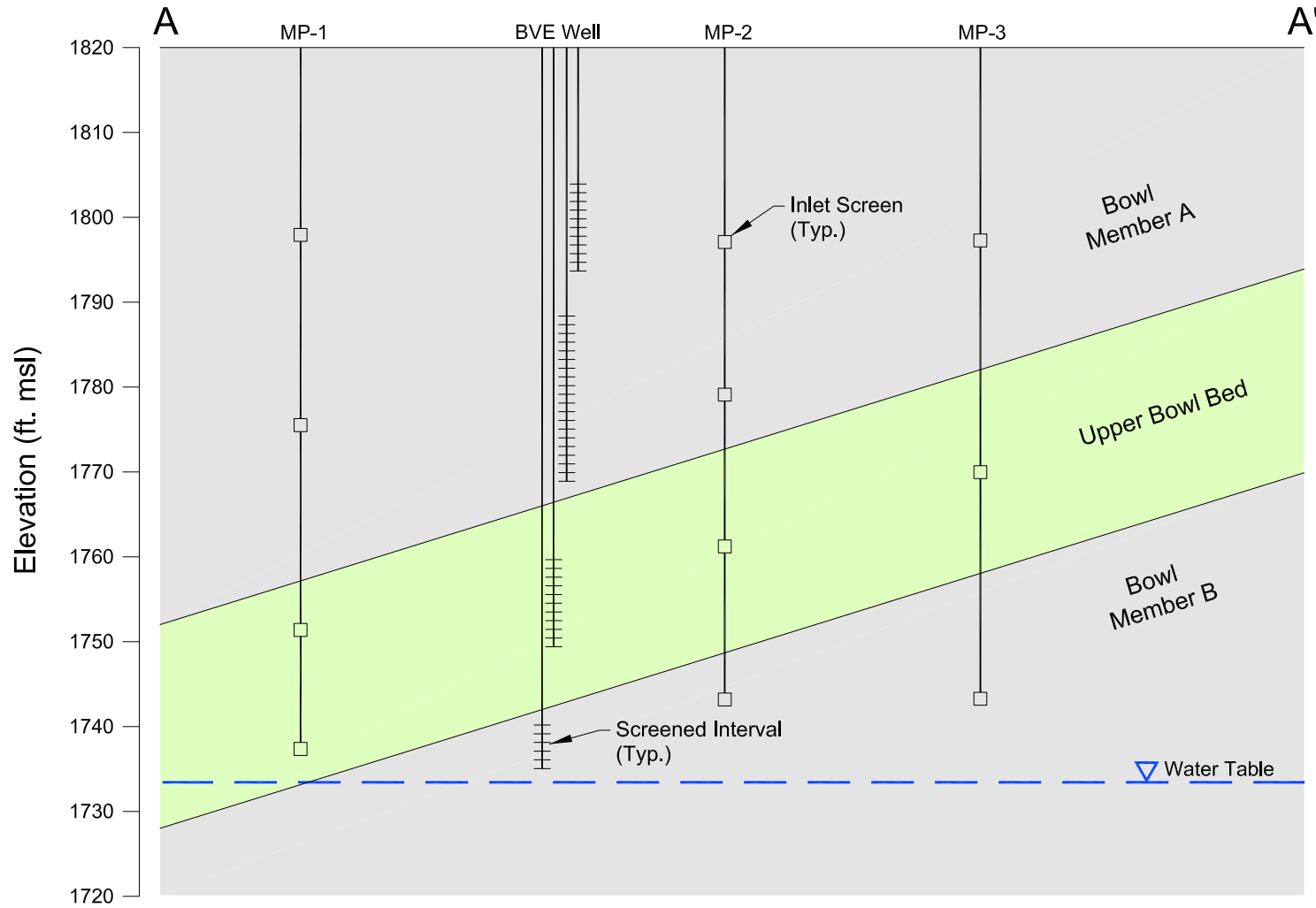
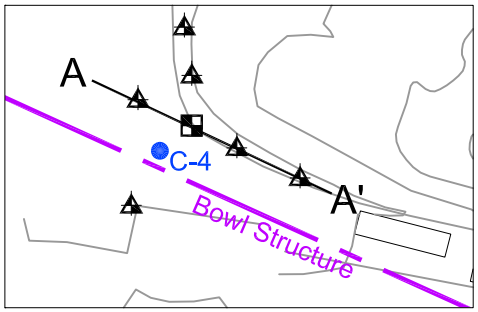
SANTA SUSANA FIELD LABORATORY
VENTURA COUNTY, CALIFORNIA
APRIL 2009

**LAYOUT OF BEDROCK VAPOR EXTRACTION WELL AND MONITORING PROBES**

FIGURE 4-1




Cross-Section Location

0 FEET 20
SCALE

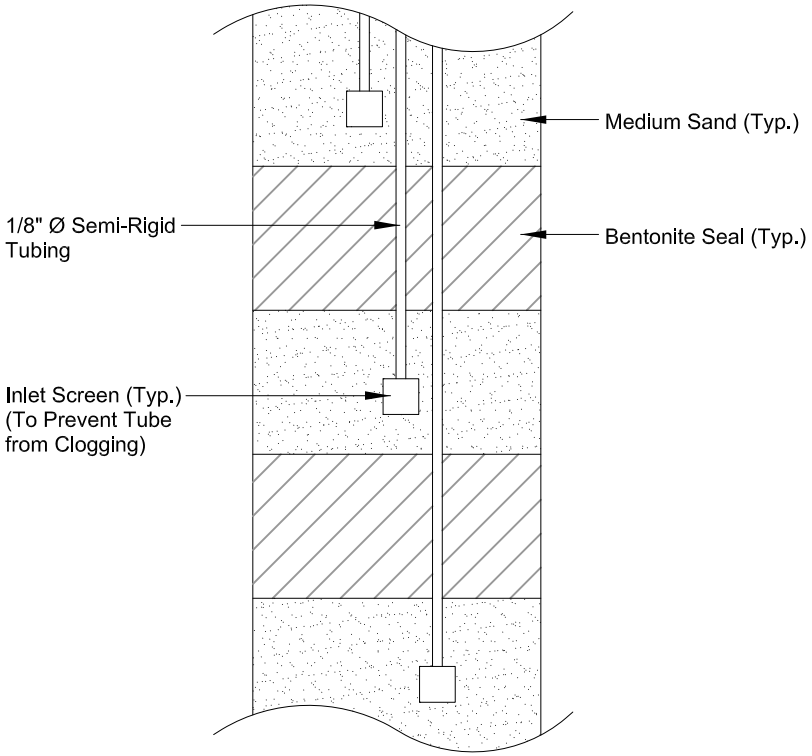
**MWH**

SANTA SUSANA FIELD LABORATORY
VENTURA COUNTY, CALIFORNIA
APRIL 2009

SCHEMATIC CROSS-SECTION OF
BVE WELL AND MONITORING PROBES

FIGURE 4-2

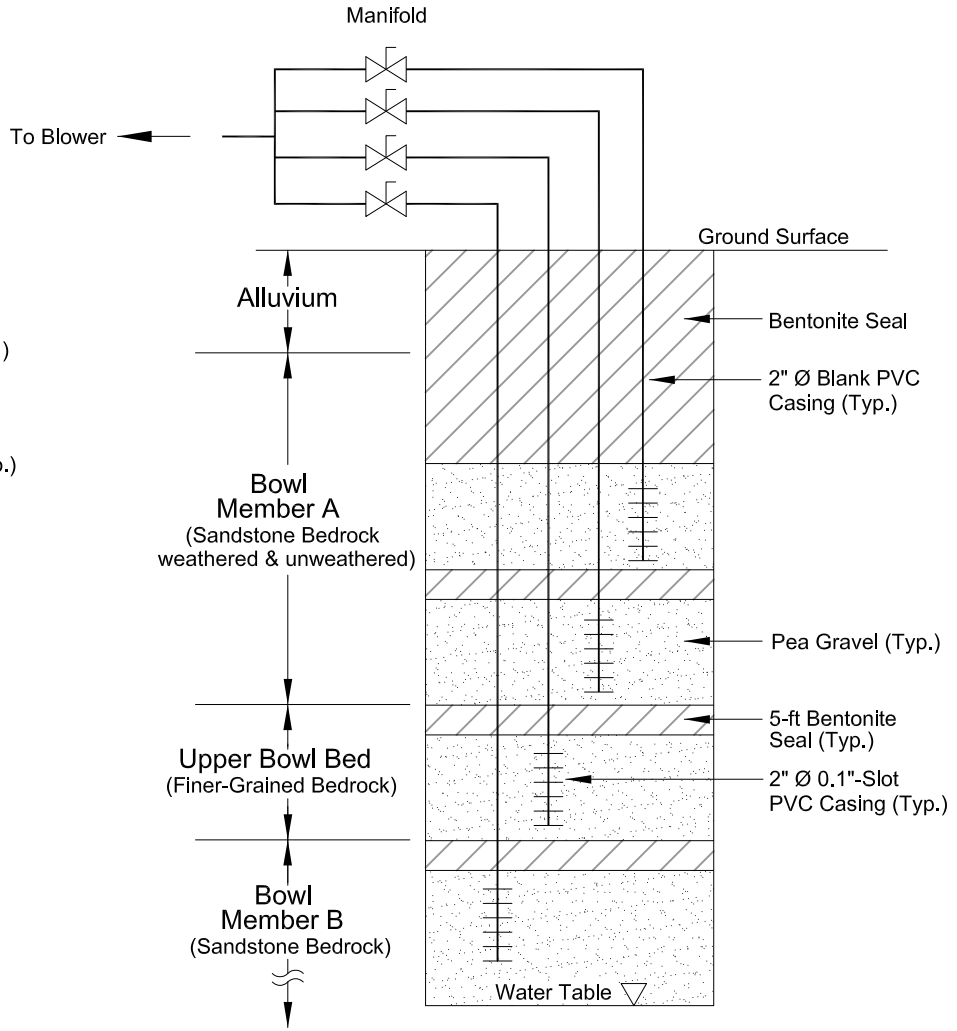
FILE No. CAD MLUEBKE\BOEING SANTA SUSANA\WORKPLAN 4 09\BVE X SECTION




## Typical Multilevel BVE Monitoring Well

Number, Depth, and Thickness of Monitoring Zones Vary Depending Upon Stratigraphy at Well Location and Monitoring Objectives.

All Tubing Strapped to 1/2" Ø PVC Pipe (To Support and Centralize) with Cable Ties and Pipe-Wrap Tape.




## Multilevel BVE Well

NOT TO SCALE

**MWH**

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VENTURA COUNTY, CALIFORNIA
APRIL 2009

*CONCEPTUAL COMPLETION DIAGRAMS, BVE WELL AND MONITORING PROBES*

FIGURE 4-3

FILE: CADMLUEBKE\BOEING SANTA SUSANA\WORKPLAN 4 09\BVE WELL DETAILS 4 6 09

# APPENDICES

## Appendix A

Technical Memorandum Conceptual Site Model Movement of TCE in the Chatsworth Formation, Appendix E Evolution of TCE Source Zones and Plumes in the Chatsworth Formation Groundwater. Montgomery Watson, 2000:

Figure 5-13 RD-35B Rock sample results expressed as TCE in pore water
Figure 5-18 RD-46B Rock core sample results expressed as TCE in pore water

Source Zone Characterization at the Santa Susana Field Laboratory: Rock Core VOC Results for Coreholes C1 through C7. Jennifer C. Hurley, Beth L. Parker, John A. Cherry University of Waterloo, Department of Earth Sciences July 2007:

Figure 52 C1 (Instrument Equipment Lab) Profile of TCE Porewater Concentrations
Figure 53 C2 (Canyon Test Area) Profile of TCE Porewater Concentrations
Figure 54 C3 (Instrument Equipment Lab) Profile of TCE Porewater Concentrations
Figure 55 C4 (Bowl Test Area) Profile of TCE Porewater Concentrations
Figure 56 C5 (Alpha Test Area) Profile of TCE Porewater Concentrations
Figure 57 C6 (Delta Test Area) Profile of TCE Porewater Concentrations
Figure 58 C7 (Expendable Launch Vehicle) Profile of TCE Porewater Concentrations

Rock Core VOC Results for Corehole C8, Source Zone Characterization at the Santa Susana Field Laboratory, Addendum Report No. 1. Jennifer C. Hurley, Steven W. Chapman and Beth Parker, University of Waterloo, Department of Earth Sciences July 2007:

Figure 8 C8 (Former Sodium Disposal Facility) Source Area Profile of Chlorinated Ethene Porewater Concentrations

Rock Core VOC Results for Corehole C9 (RD-84), Source Zone Characterization at the Santa Susana Field Laboratory, Addendum Report No. 3. Jennifer C. Hurley and Beth Parker, University of Waterloo, in Partnership with Waterloo Hydrogeologic, Inc. Department of Earth Sciences July 2007:

Figure 8 C9 (B1 Test Area) Source Area Profile of Chlorinated Ethene Porewater Concentrations

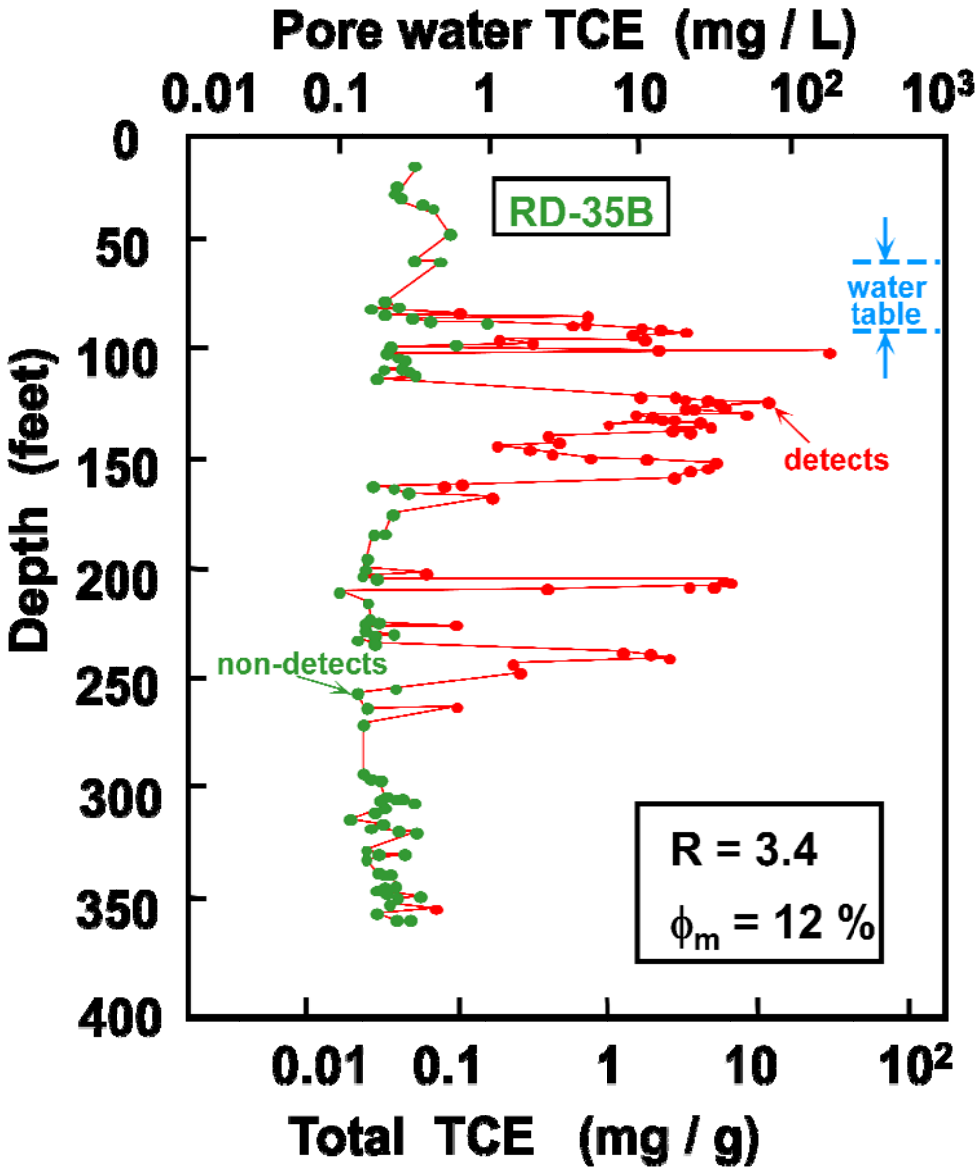
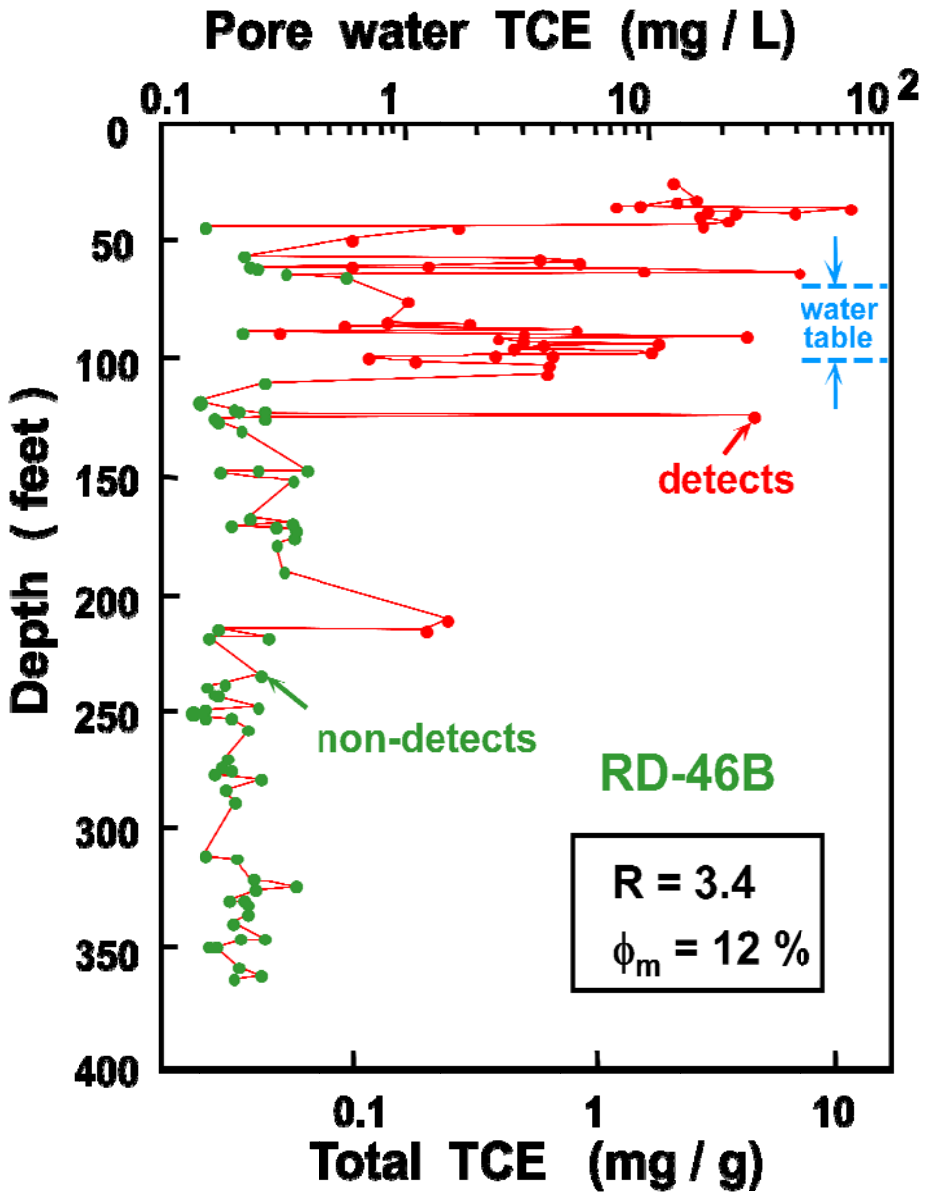



**Figure 5-13: RD-35B rock core sample results expressed as TCE in porewater (Sterling, 1999)**




**RD-46B Rock sample results expressed as TCE in pore water (Sterling 1999)**

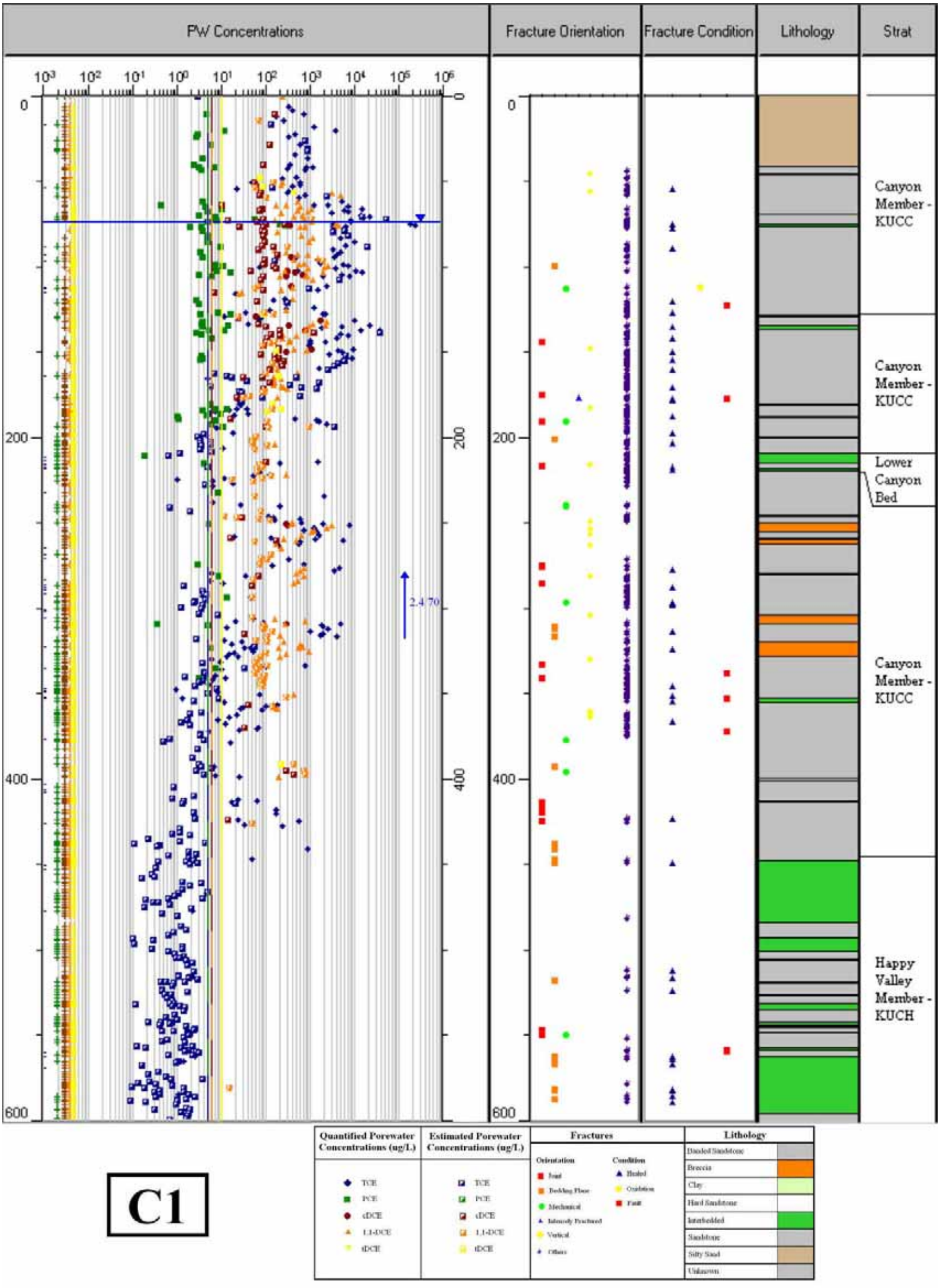



**Figure 52. C1 (Instrument Equipment Lab) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater).

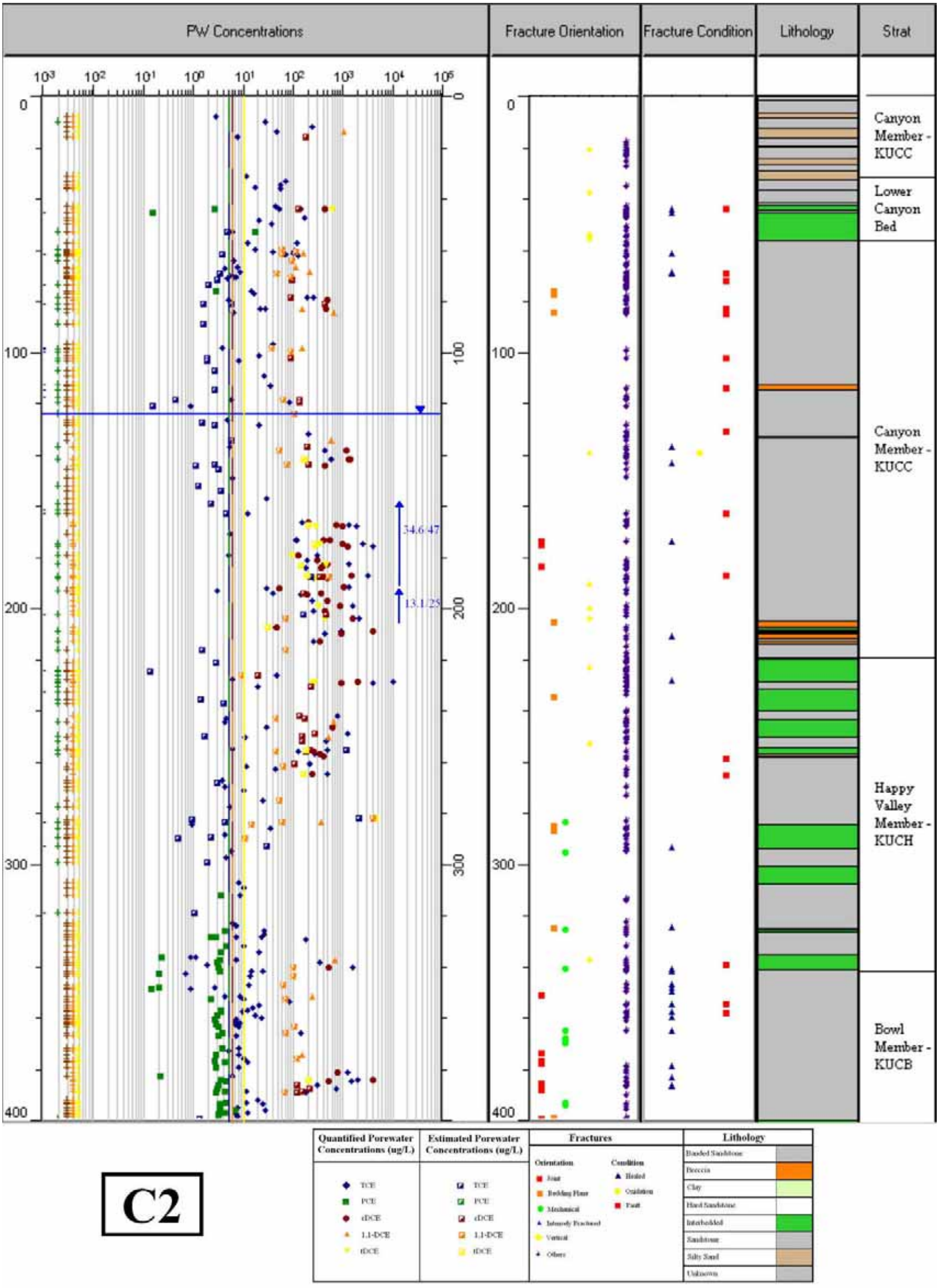



**Figure 53. C2 (Canyon Test Area) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater).

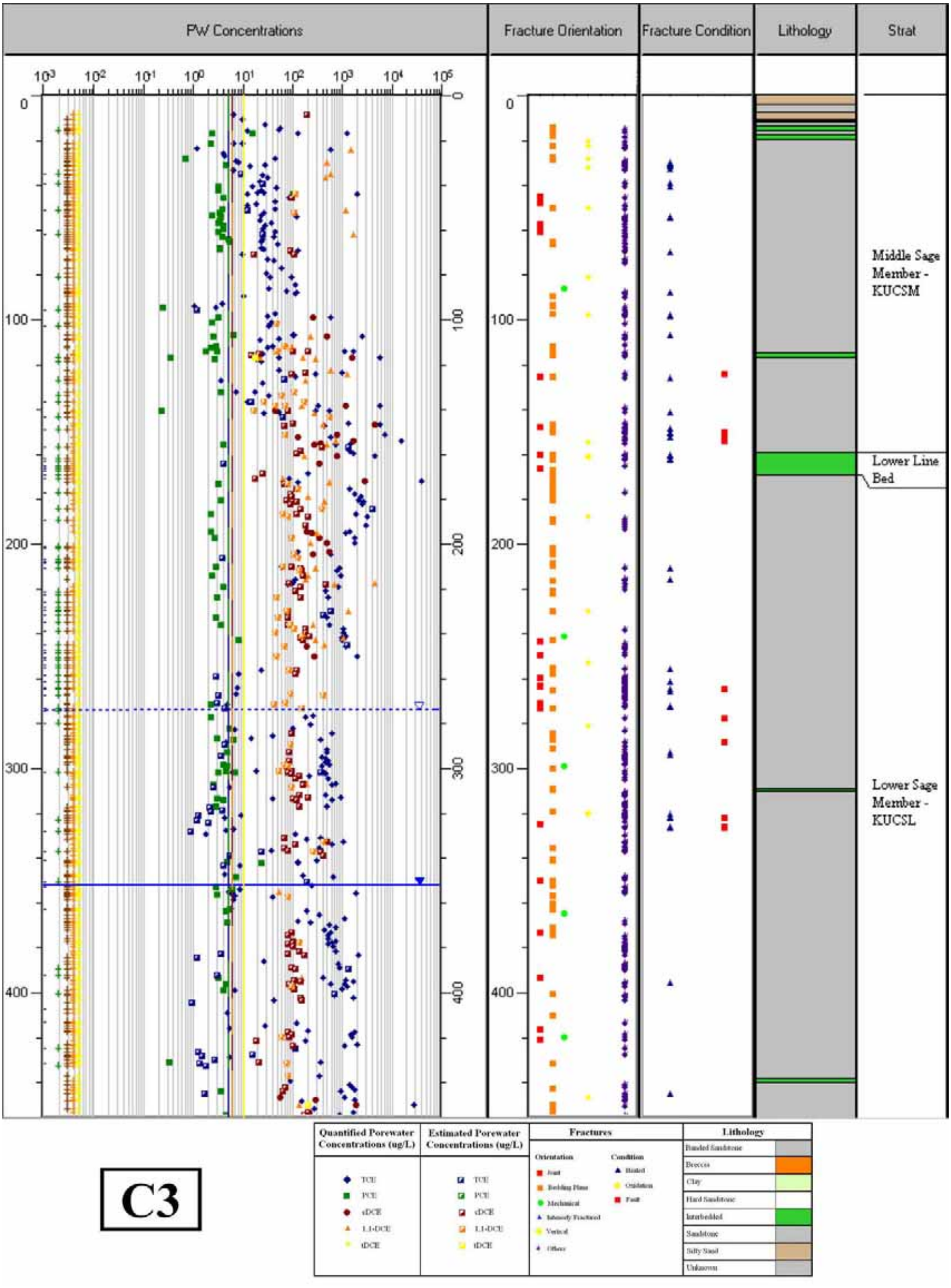



**Figure 54. C3 (Component Test Lab I) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater).

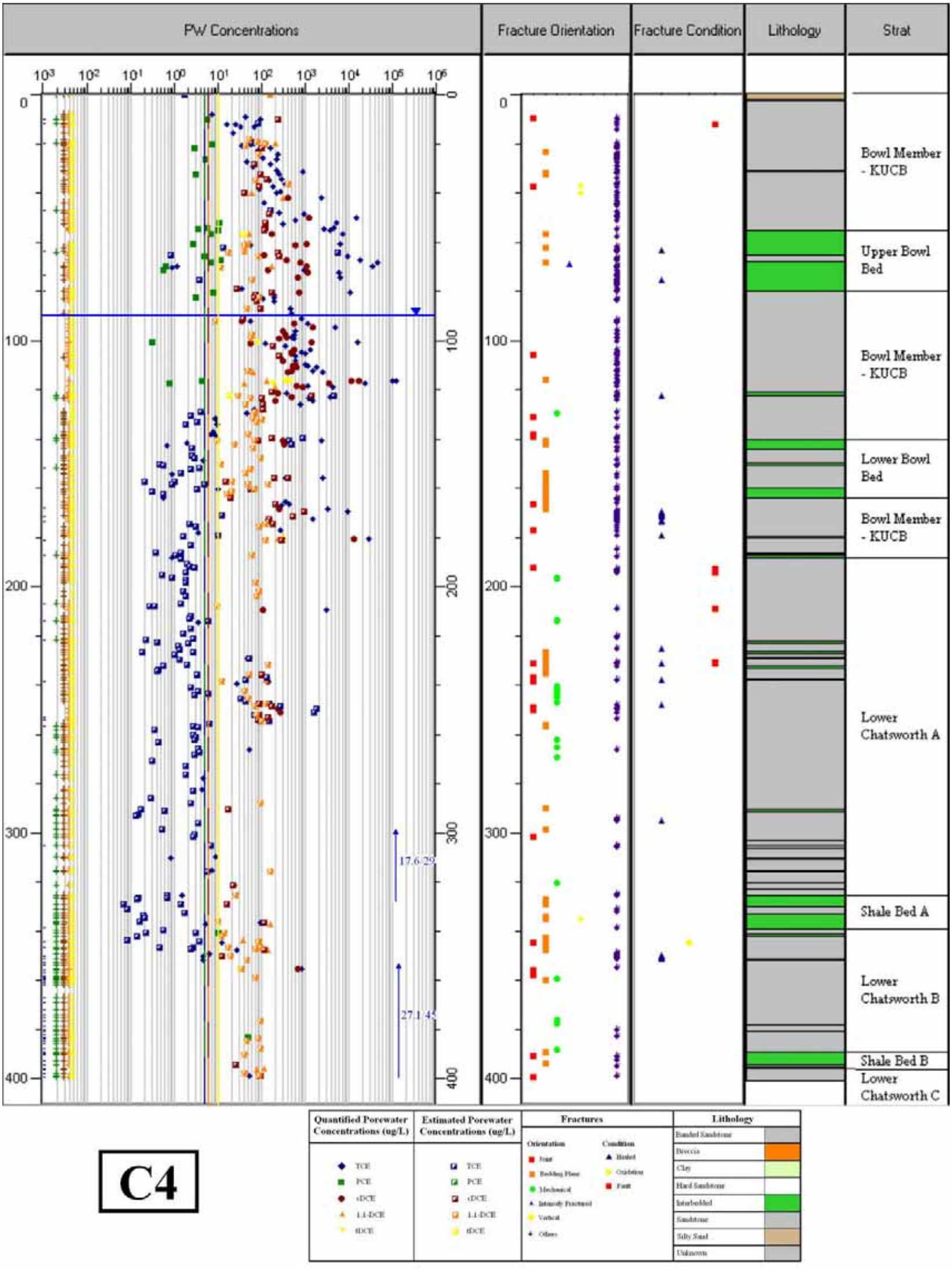



**Figure 55. C4 (Bowl Test Area) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater).

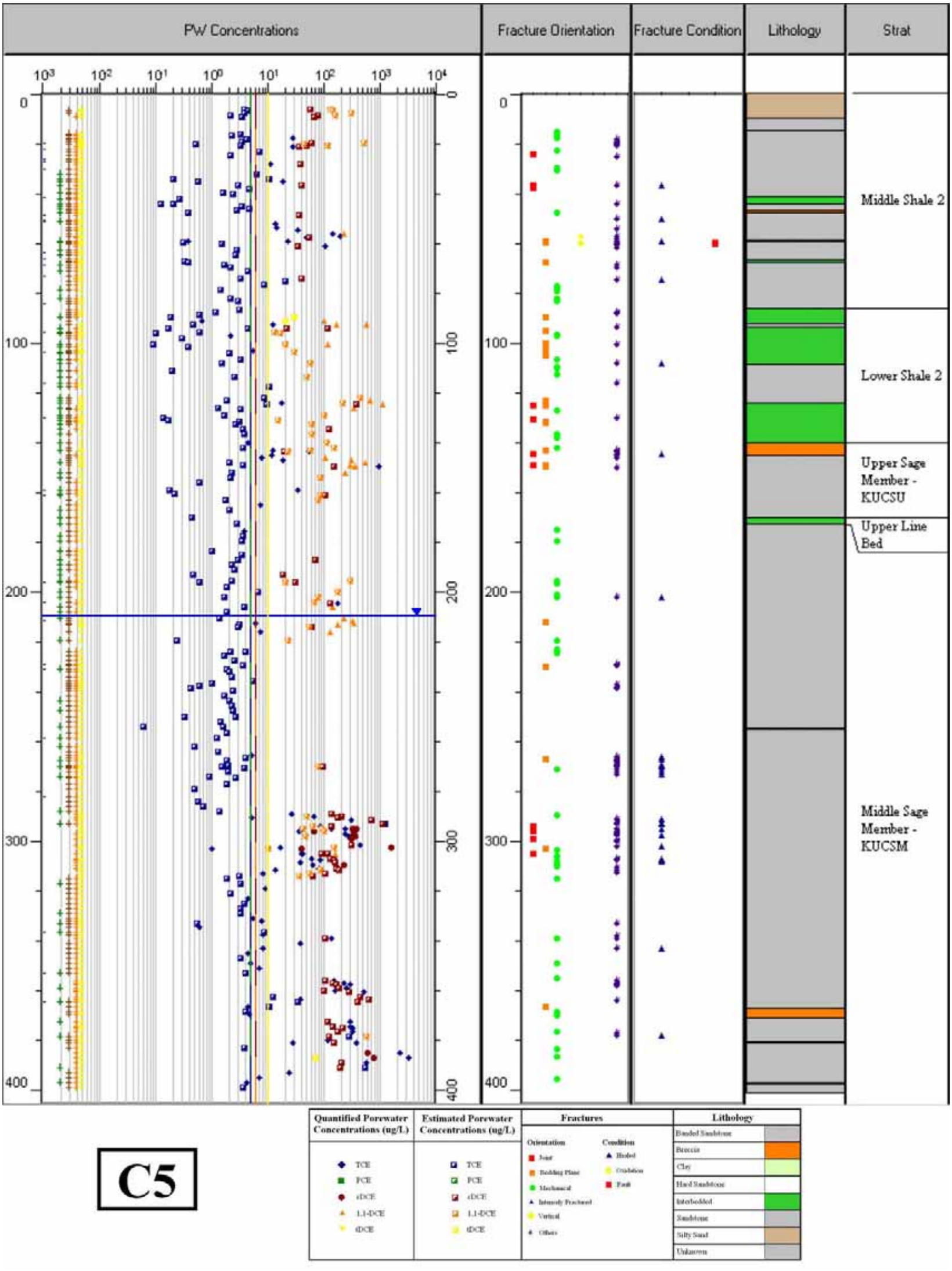



**Figure 56. C5 (Alfa Test Area) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater).

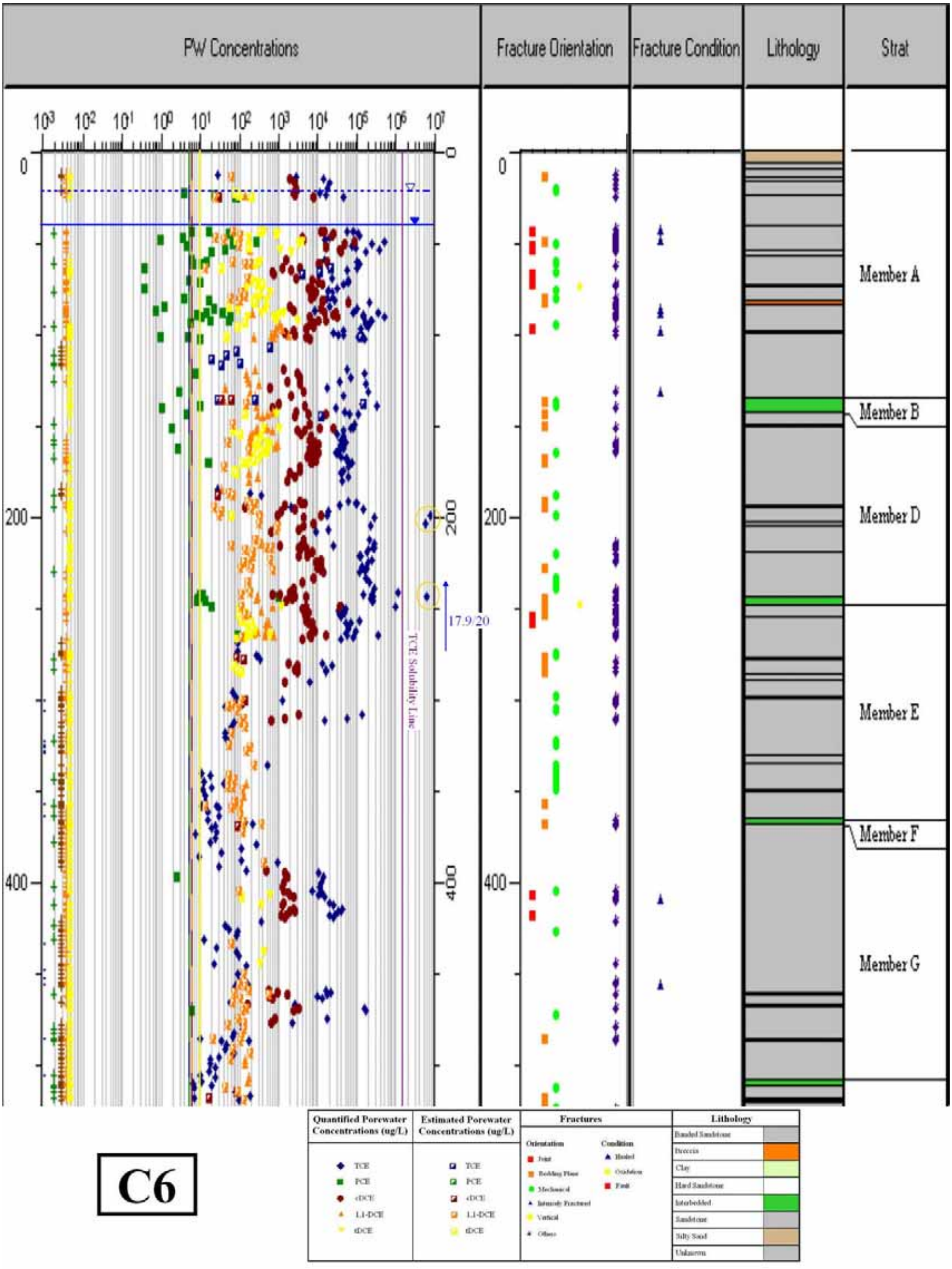



**Figure 57. C6 (Delta Test Area) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. Three samples are above TCE solubility (~$1.4 \times 10^6$ µg/L porewater), as circled on the plot.

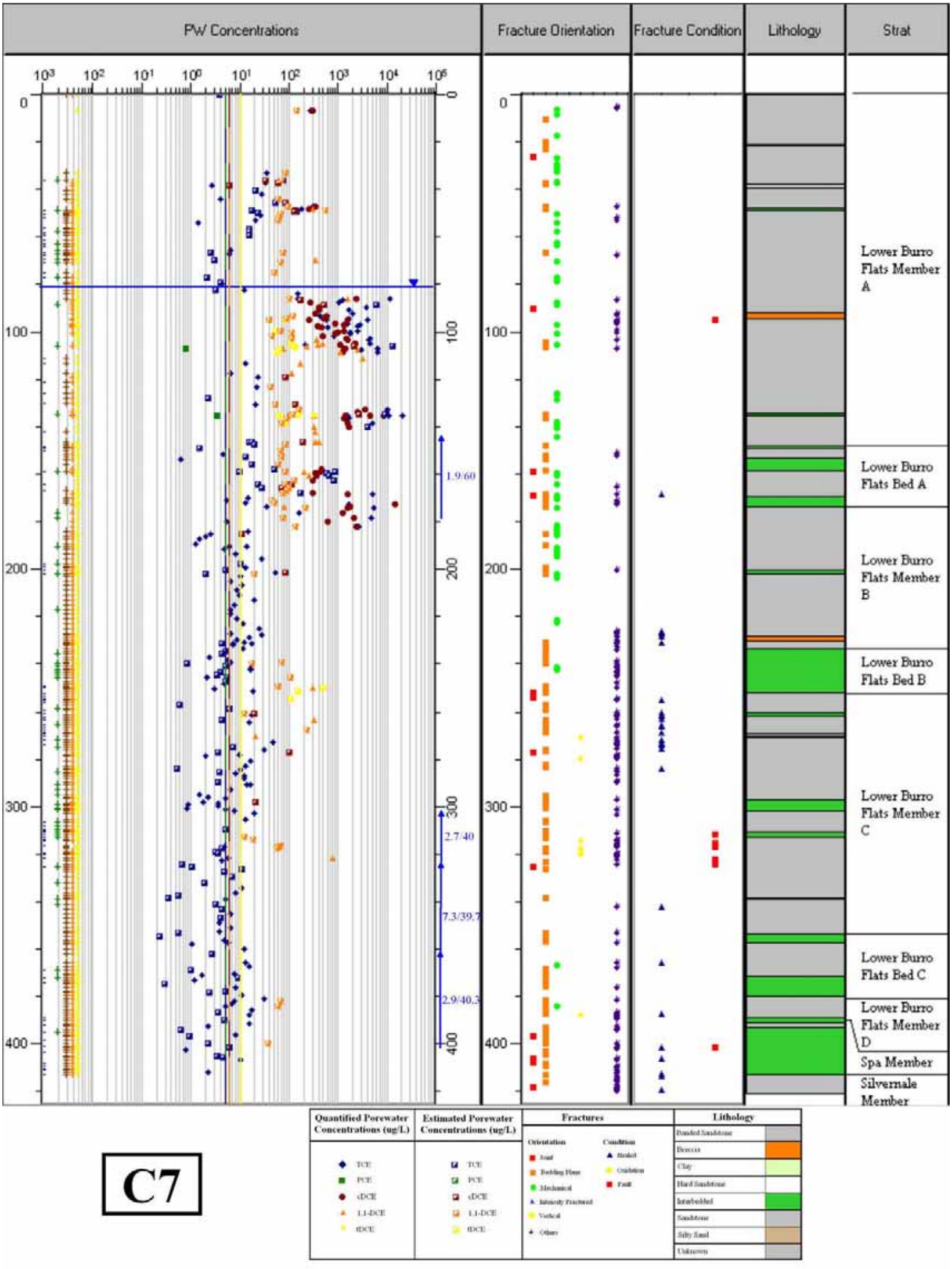



**Figure 58. C7 (Expendable Lunch Vehicle) Profile of TCE Porewater Concentrations**

Solid lines represent analyte maximum contaminant levels for drinking water for the state of California. Open symbols represent values that are estimates (fall between the method detection limit and the method reporting limit. Solid symbols represent quantitative values. Non-detects are not plotted. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater).

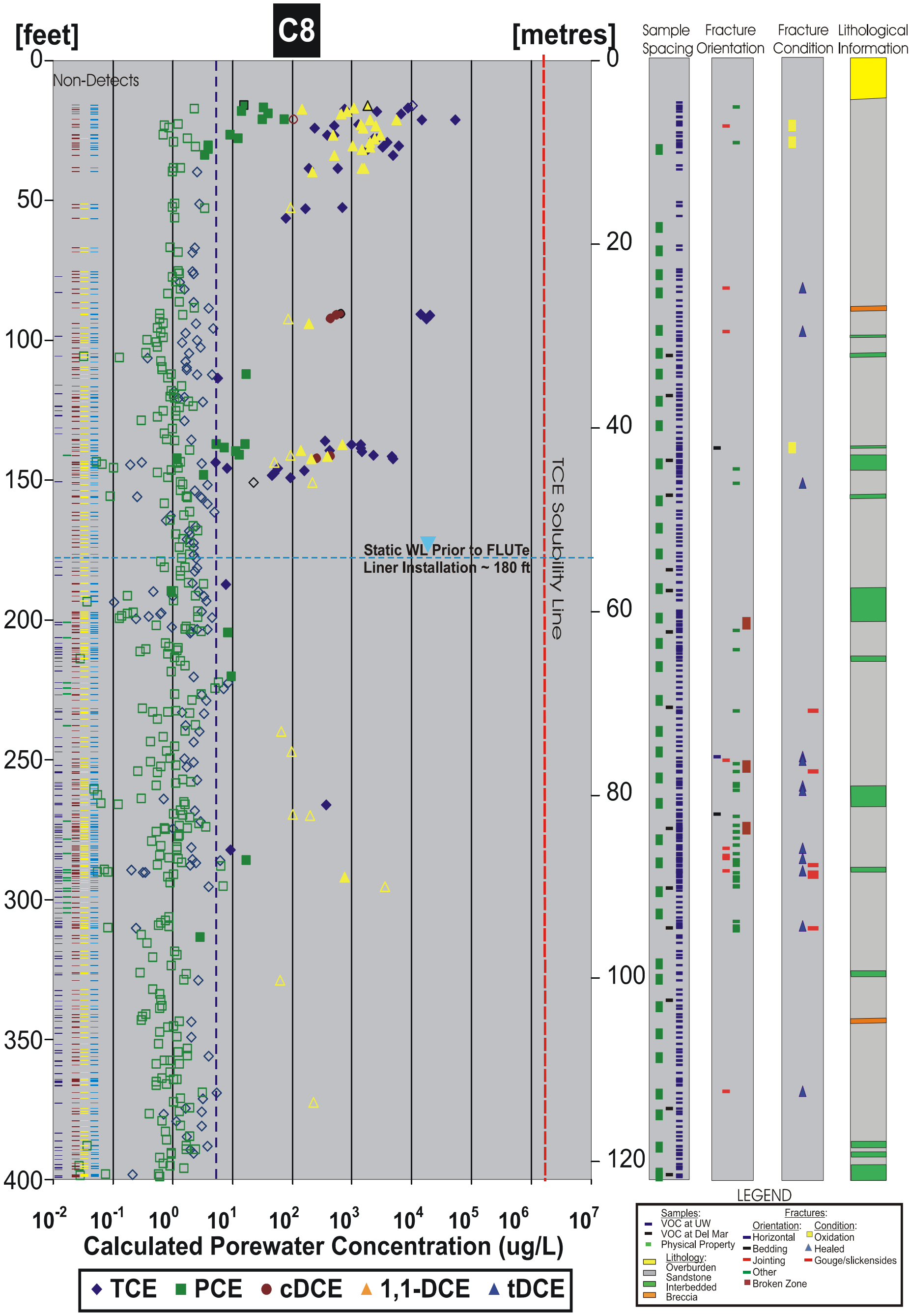



**Figure 8. C8 (Former Sodium Disposal Facility) Source Area Profile of Chlorinated Ethene Porewater Concentrations**

The dashed blue line represents the maximum TCE concentration in drinking water for the state of California. Open symbols represent values that are estimated (fall between the method detection limit and the method reporting limit) or samples that were qualified or samples that were qualified with a J flag according to the U.S EPA National Functional Guidelines for Organic Data Review (1999). Solid symbols represent quantitative values. Non-detects are shown as dashes along the left margin.

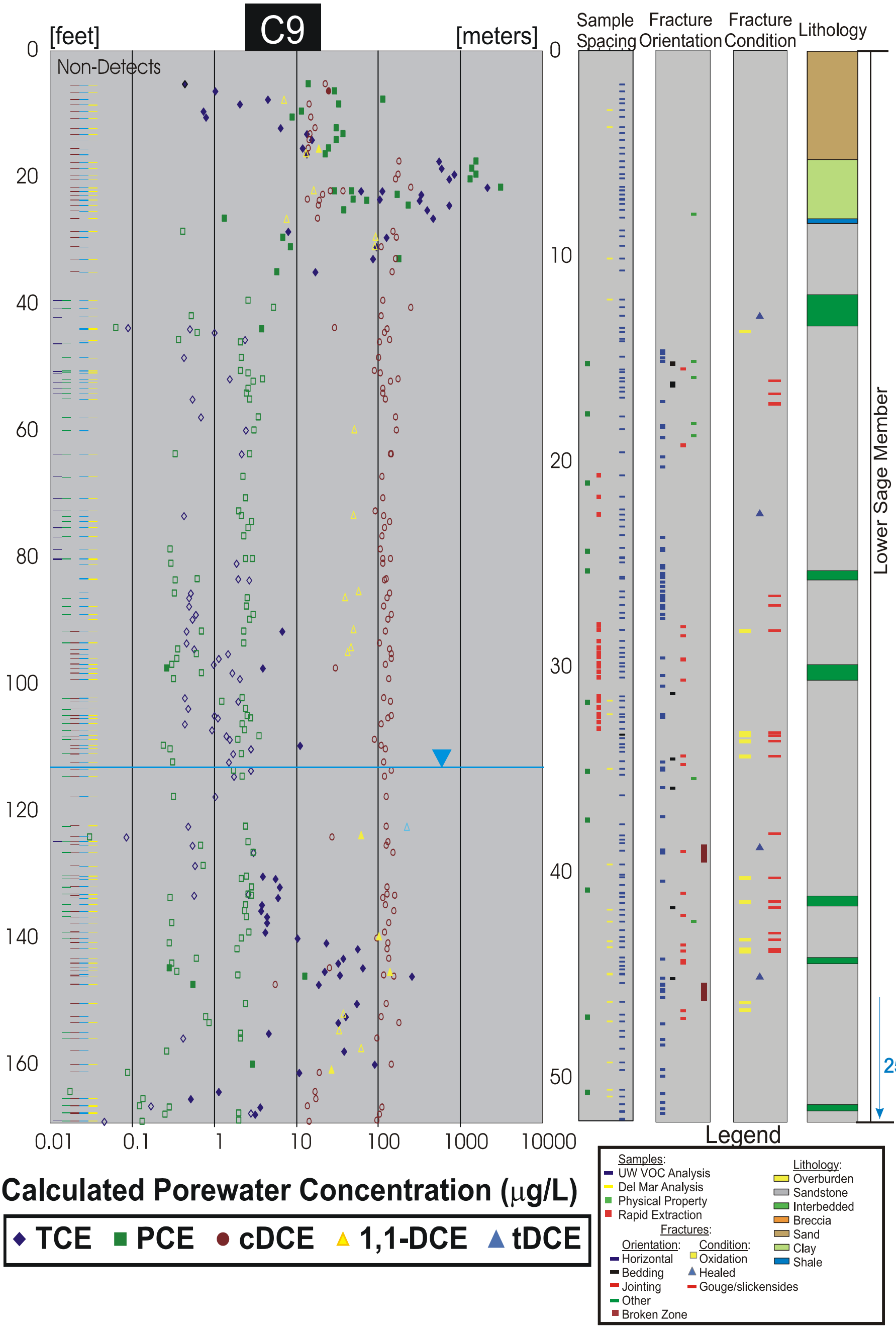



**Figure 8. C9 (B1 Test Area) Profile of Chlorinated Ethene Porewater Concentrations**

The dashed blue line represents the maximum TCE concentration in drinking water for the state of California. Open symbols represent values that are estimated (fall between the method detection limit and the method reporting limit) or samples that were qualified or samples that were qualified with a J flag according to the U.S EPA National Functional Guidelines for Organic Data Review (1999). Solid symbols represent quantitative values. Non-detects are shown as dashes along the left margin. All concentrations are below TCE solubility (~$1.4 \times 10^6$ µg/L porewater). A strong downward hydraulic gradient was observed in the bottom of the corehole from 148 to 171 ft bgs.

# TREATABLILITY STUDY WORK PLANS
# SANTA SUSANA FIELD LABORATORY
# VENTURA COUNTY, CALIFORNIA

## *APPENDIX B*
## *IN SITU* CHEMICAL OXIDATION FIELD EXPERIMENT
## *SANTA SUSANA FIELD LABORATORY*

**Prepared For:**

**THE BOEING COMPANY**
**The NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
**and**
**The UNITED STATES DEPARTMENT OF ENERGY**

**Prepared By:**

**MWH**
**618 Michillinda Avenue Suite 200**
**Arcadia, CA 91007**

**June 2009**

# WORK PLAN
# *IN SITU* CHEMICAL OXIDATION FIELD EXPERIMENT
# SANTA SUSANA FIELD LABORATORY

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**VENTURA COUNTY, CALIFORNIA**

**Prepared For:**

**The Boeing Company**
**The National Aeronautics and Space Administration**
**The United States Department of Energy**

**Prepared By:**

**MWH**
**2121 North California Blvd.**
**Suite 600**
**Walnut Creek, California 94596**

**June 2009**

MWH

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## ABBREVIATIONS AND ACRONYMS

| | |
|---|---|
| bgs | below ground surface |
| Boeing | The Boeing Company |
| β-$MnO_2$ | pyrolusite |
| $^oC$ | degrees Celsius |
| $C_2HCl_3$ | trichloroethene |
| $C_2H_2Cl_2$ | dichloroethene |
| $C_2H_3Cl$ | vinyl chloride |
| $Cl^-$ | chloride ion |
| $CO_2$ | carbon dioxide |
| DCE | dichloroethene |
| DOE | United States Department of Energy |
| DTSC | Department of Toxic Substances Control |
| $e^-$ | electron |
| $Fe(OH)_2$ | ferrous hydroxide |
| $FeS_2$ | pyrite |
| g/L | gram per liter |
| $g/m^2$ | gram per square meter |
| gpm | gallons per minute |
| $H^+$ | hydrogen ion |
| $H_2O$ | water |
| HASP | Health and Safety Plan |
| IEL | Instrument and Equipment Laboratory |
| HASP | Health and Safety Plan |
| $K^+$ | potassium ion |
| $KMnO_4$ | potassium permanganate |
| LARWQCB | Los Angeles Regional Water Quality Control Board |
| $MnO_2$ | manganese dioxide |
| $MnO_4^-$ | permanganate ion |
| msl | above mean sea level |
| MWH | MWH Americas, Inc. |
| $Na^+$ | sodium ion |

## ABBREVIATIONS AND ACRONYMS (continued)

| | |
|---|---|
| $Na_2S_2O_8$ | sodium persulfate |
| NASA | National Aeronautics and Space Administration |
| NOD | natural oxidant demand |
| $OH^-$ | hydroxyl ion |
| ORP | oxidation-reduction potential |
| Panel | Groundwater Advisory Panel |
| PPE | personal protective equipment |
| RCRA | Resource Conservation and Recovery Act |
| RFI | RCRA Facility Investigation |
| $S^{2-}$ | sulphur ion |
| SCM | Site Conceptual Model |
| SEM/EDS | Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy |
| $SO_4^-$ | sulphate |
| SSFL | Santa Susana Field Laboratory |
| TCE | trichloroethene |
| µg/L | micrograms per liter |
| USEPA | United States Environmental Protection Agency |
| VC | vinyl chloride |
| VCFPD | Ventura County Fire Protection Division |
| VOC | volatile organic compound |
| **WDR** | Waste Discharge Requirements |

# 1.0 INTRODUCTION

This work plan presents design criteria for the implementation and evaluation of in situ chemical oxidation to address target contaminants in Chatsworth formation[1] groundwater beneath the Santa Susana Field Laboratory (SSFL). *In situ* chemical oxidation was identified as a candidate technology for a field experiment in the technical memorandum titled *Preliminary Evaluation of Groundwater Remediation Technologies at the SSFL* which was included in Appendix D of the Feasibility Study Work Plan (MWH, 2009b).

## 1.1 BACKGROUND INFORMATION

The SSFL is located in the southeast corner of Ventura County, 29 miles northwest of downtown Los Angeles, California. The location of the SSFL and its surrounding vicinity is shown on Figure 1-1. The SSFL is jointly owned by Boeing and the federal government (administered by the National Aeronautics and Space Administration [NASA]) and is operated by The Boeing Company (Boeing). The United States Department of Energy (DOE) used a portion of the SSFL. However, there are no longer any active DOE operations and the facilities are undergoing decommissioning and demolition. This work plan has been prepared by MWH Americas, Inc. (MWH) on behalf of Boeing, NASA and DOE.

Previous environmental investigations have shown that the Chatsworth formation beneath portions of the SSFL has been impacted by releases of chemicals from historical operations, with trichloroethene (TCE) being the compound detected at the highest concentration and with the greatest frequency. The occurrence of TCE in groundwater beneath the SSFL was first reported in early 1984 when on-site water supply wells were sampled and analyzed for the presence of TCE and other volatile organic compounds (VOCs). Groundwater characterization studies at the SSFL using conventional fractured rock methods have been ongoing since about 1985.

The Groundwater Advisory Panel (Panel) was commissioned in 1997 to develop a groundwater site conceptual model (SCM) describing the movement of chemicals of potential concern in the Chatsworth formation. At the recommendation of the Panel, new methods including rock coring

[1] The Chatsworth formation constitutes the bedrock that lies beneath the SSFL and consists predominantly of fractured sandstone.

and crushing were used to characterize TCE in the fractured sedimentary rock of the Chatsworth formation during the late 1990's. In April 2000, a technical memorandum was submitted to the Department of Toxic Substances Control (DTSC) that presented the site conceptual model describing TCE movement in the Chatsworth formation (Montgomery Watson, 2000). The SCM was based on the Panel's understanding of TCE solute transport in fractured sedimentary rock (e.g., Chatsworth formation) and the available data as of late 1999.

Additional field studies have been performed since late 2000 to characterize groundwater at the SSFL consistent with work plans submitted to DTSC. The work involved applying both conventional and new investigation methods including retrofitting existing wells with multi level monitoring systems, analysis of rock cores for select VOCs and physical properties, and various methods of geophysical, hydrophysical and aquifer testing. Much of the data that were collected and analyzed since 2000 were evaluated and incorporated into an update of the groundwater SCM for contaminant transport (Cherry, et. al, 2007).

## 1.2 WORK PLAN OBJECTIVE

The objectives of this work plan are to select an appropriate oxidant and test location and design a field experiment to assess the effectiveness of *in situ* chemical oxidation within the Chatsworth formation aquifer. Effectiveness will be measured by evaluating a set of six performance criteria including: the delivery and distribution of the oxidant; the extent of oxidation of TCE and its daughter products 1,1-dichloroethene (DCE), cis-1,2-DCE, trans-1,2-DCE, and vinyl chloride (VC) within the fracture system and rock matrix; the magnitude of contaminant reduction in the rock matrix; the natural oxidant demand (NOD) of organic and inorganic constituents present in the Chatsworth formation; the magnitude and extent of mineral deposits on the solid surfaces of the rock associated with the oxidation reaction; and the potential for manganese and iron oxide precipitation in the fracture system and rock matrix.

Performance criteria will be assessed by monitoring hydrologic, geochemical, and geophysical properties in the field experiment area. Monitoring data including groundwater quality parameters and contaminant concentrations will be collected from a network of local monitoring wells. Data will also be collected from rock surfaces and pore water in the rock matrix by drilling and sampling rock cores. Based on the assessment of the performance criteria, this technology will be given further consideration in the feasibility study for the SSFL.

Section 2.0 of this work plan summarizes the site conditions including the geologic setting and occurrence and distribution of TCE in the Chatsworth formation beneath the field experiment area. Section 3.0 presents the basis for and selects the most appropriate oxidant for the field experiment, defines the performance criteria for evaluation of the experiment, and outlines the injection scheme, injection system equipment, and monitoring program. Section 4.0 addresses health and safety, Section 5.0 addresses permitting, Section 6.0 describes the final report and Section 7.0 proposes a schedule for the field experiment design and implementation.

## 2.0 *IN SITU* CHEMICAL OXIDATION FIELD EXPERIMENT LOCATION

Sixteen areas of primarily TCE-impacted groundwater have been identified at the SSFL and are shown on Figure 2-1. These areas are labeled 1, 3 through 13, and 15 through 18. Each of these areas was considered as a potential location for conducting the *in situ* chemical oxidation field experiment and was evaluated for its suitability based on a set of preferred characteristics describing the impacted groundwater areas. A summary of the characteristics and evaluation is presented in Appendix D of the Feasibility Study Work Plan (MWH, 2009b). Based on the evaluation, the Instrument and Equipment Laboratory (IEL) Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) Site was selected to conduct the field experiment and well RD-35A was selected as the injection well.

One of the primary reasons for selecting the field experiment location at the IEL RFI Site was due to the extensive amount of research and data collected in the northeast area. Six rock core investigation holes (C-11, C-10, RD-35B, RD-35C, C-1 and RD-31) have been drilled in and around the IEL RFI Site for the purpose of collecting contaminant distribution, geophysical, geochemical, and geologic data for groundwater characterization in the northeast portion of the SSFL. The coreholes, shown in Figure 2-2, are oriented southeast-northwest and transect the area of impacted groundwater beneath the field experiment location.

Detailed information regarding the geology, hydrogeology, and contaminants present in the groundwater beneath the field experiment test area at the IEL RFI Site is presented in the following reports:

- Integration Report on the Intensive Studies Conducted at Monitoring Sites RD-35 and RD-46 at the Santa Susana Field Laboratory, Ventura County, California (Cherry, et. al, 1999)
- Phase 1 Northeast Area Groundwater Characterization Report (MWH, 2004)
- Revised Source Zone Characterization at the Santa Susana Field Laboratory: Rock Core VOC Results for Coreholes C1 through C7 (Hurley, et. al, 2007)
- Phase 2 Northeast Area Groundwater Characterization Technical Memorandum (Parker, et. al, 2008)
- Site-wide Groundwater Characterization Work Plan (MWH, 2008)
- Group 1A RCRA Facility Investigation Report, Appendix J – Chemicals in Groundwater (MWH, 2009a)

## 2.1 GEOLOGY

The Chatsworth formation underlying the field experiment location includes three coarser-grained members consisting primarily of sandstone (the Bowl Member, Canyon Member, and Sage Member) and two finer-grained members which contain higher percentages of siltstones and shales (the Happy Valley Member, Woolsey Canyon Member). Proposed injection well RD-35A is located entirely within the Canyon Member. Coreholes RD-35B, RD-35C, C-1, and RD-31 are located on the eastern side of the Shear Zone and therefore penetrate the same stratigraphic sequence, beginning with the Canyon Member, which outcrops at the surface, and proceeding through the finer-grained Happy Valley Member and into the Bowl Member. Corehole C-10 is on the eastern side of the Shear Zone, located close to the fault where the Canyon Member is thickest. As a result, the entire length of corehole is within the Canyon Member. Corehole C-11 was drilled on the western side of the Shear Zone and intersects different, younger stratigraphic units. The corehole intersects the following stratigraphic sequence (from youngest to oldest): Upper Sage member, the Upper Line bed, the Middle Sage member, the Lower Line bed, the Lower Sage member, and the Woolsey member. Locations of surrounding wells and coreholes in relation to geologic features in the field experiment area are shown on Figure 2-2 and a cross-section of the coreholes within the various stratigraphic units is depicted on Figure 2-3.

Five major lithology types were identified in the coreholes beneath the field experiment location including: sandstone, hard sandstone, banded sandstone, breccias, and interbedded siltstone (consisting of siltstone, sandstone, and shale).

Several faults have been identified in the field experiment area including the Woolsey Canyon Fault to the north, Happy Valley Fault to the south, and the IEL Fault to the southeast of the test area. The Shear Zone is a fault that strikes northeast-southwest and borders the field experiment area on the northwest.

## 2.2 HYDROGEOLOGY

Depth to Chatsworth formation groundwater in the field experiment area ranges from 40 feet below ground surface (bgs) at HAR-16 in the south to over 100 feet bgs near the Woolsey Canyon Fault to the north. Depth to water in well RD-35A has ranged from 57 feet to 91 feet bgs. West of the Shear Zone, the depth to first groundwater is over 300 feet bgs and is

believed to be the result of historical groundwater pumping operations from supply wells located on the west side of the Shear Zone.

Chatsworth formation groundwater elevations and flow directions beneath the field experiment test area appear to be largely influenced by topography and the presence of faults and finer-grained lithologic units. Based on the distribution of chemical impacts (which are tracers of the flow system), the net lateral movement of Chatsworth formation groundwater beneath the test area appears to be towards the northeast and parallel to the Shear Zone, which is a dominant low bulk hydraulic conductivity structure in the northeastern SSFL. The Happy Valley Member also appears to have an observable influence on the groundwater system in this area, as discrete-depth hydraulic head measurements collected from Westbay multilevel monitoring systems at RD-31 and RD-35C show that the piezometric elevation drops by approximately 50 feet across this lithologic unit.

## 2.3 OCCURRENCE AND DISTRIBUTION OF TCE IN THE BEDROCK AND GROUNDWATER

The source of TCE and other chlorinated VOCs at the IEL RFI Site is primarily from chlorinated solvent use associated with laboratory operations. Potential input locations within the IEL RFI Site boundary included the Acid Bay, a clarifier and subsurface pipeline connecting the clarifier to a leach field, two underground waste solvent storage tanks, and several solvent degreaser units. Operations involving chlorinated solvents were conducted at the IEL RFI Site from the late 1940s until 2006 (MWH, 2009a). Figure 2-2 shows TCE iso-concentration contours in groundwater around the field experiment location.

The extent of TCE in the bedrock matrix beneath the field experiment location was evaluated and summarized in the Phase 2 Northeast Area Groundwater Characterization Technical Memorandum (Parker, et. al, 2008). More than 2,300 samples were collected from the six coreholes in the area proposed for the field experiment and analyzed for sorbed, dissolved, and immiscible phase chlorinated ethenes. Lithologic properties including matrix porosity, fraction of organic carbon, and wet and dry bulk densities of the rock matrix were used to calculate pore water TCE concentrations from the rock core sample concentrations. DCE isomers cis-1,2-DCE, trans-1,2-DCE, and 1,1-DCE detected in the rock core samples were assumed to be derived from the transformation of TCE. For each sample, the DCE isomer concentrations were converted to

equivalent moles of TCE, added to the measured TCE concentration, and termed equivalent TCE concentrations.

Previous rock core sample results obtained from coreholes C-1 and RD-35B had maximum calculated pore water concentrations of 220,000 micrograms per liter (µg/L) and 110,000 µg/L, respectively. During the Phase 2 groundwater characterization work, corehole C-10 had the highest calculated TCE concentrations in pore water of the four coreholes that were drilled along the source zone transect. Corehole C-10 had TCE concentrations up to 22,000 µg/L in pore water while C-11 contained minimal mass and had a maximum concentration of 15 µg/L in pore water. Corehole RD-35C, nearest to the proposed injection location, had a maximum TCE concentration of 6,400 µg/L in pore water. Total equivalent TCE concentrations in pore water in each corehole were plotted by depth to show vertical distribution and are depicted on Figure 2-4.

The total equivalent TCE mass within the transect coreholes ranged from 185 grams per cubic meter ($g/m^2$) for combined nested coreholes RD-35B/C to 43 $g/m^2$ in corehole C-10. Immediately across the Shear Zone from C-10, the total equivalent TCE mass in corehole C-11 was less than 0.02 $g/m^2$ indicating that the Shear Zone acts as a hydraulic barrier and minimizes the TCE flux across it. The equivalent TCE mass profiles indicate coreholes RD-35B/C and C-1 are located in the source area while C-10 and RD-31 are located on the northwest and southeast fringes.

Cumulative equivalent TCE concentrations were also plotted by depth and are depicted on Figure 2-5. The cumulative mass profiles for two of the coreholes, C-1 and RD-31, show decreases in the rate of mass accumulation associated with the occurrence of the finer-grained Happy Valley member. In particular, RD-31 shows an order of magnitude decrease in TCE concentrations from above the Happy Valley member to within the Happy Valley member.

## 2.4 INJECTION LOCATION

Well RD-35A was selected as the injection well for the *in situ* chemical oxidation field experiment. RD-35A is located at the IEL RFI Site, which contains some of the highest concentrations and equivalent TCE mass measured at the SSFL, and is centrally located within an extensive array of monitoring intervals that will support monitoring during the field experiment. The maximum historic TCE concentration measured in groundwater collected from the open borehole at RD-35A was 110,000 µg/L, although more recent data indicates that concentrations are nearly an order of magnitude lower. Figure 2-6 summarizes groundwater

elevations and chlorinated ethene data collected from RD-35A since 1993. Figure 2-7 depicts the cumulative equivalent TCE mass profile for the combined data set from RD-35B and RD-35C coreholes, both of which are located adjacent to RD-35A. The data show that the greatest rate of mass accumulation occurs from 100 to 150 feet bgs, within and immediately below the screened interval of RD-35A.

RD-35A currently has a total depth of 105 feet bgs and a screened interval from 65 feet to 105 feet bgs. The most recent depth to water measured in RD-35A was 91 feet bgs. In order to be used as the injection well in the field experiment, the casing in RD-35A will be drilled out and the well will be re-drilled to 150 feet bgs. A 10-inch diameter conductor casing will be installed from ground surface to 100 feet bgs and an 8-inch diameter open borehole from 100 feet to 150 feet bgs will be used for injection.

# 3.0 *IN SITU* CHEMICAL OXIDATION FIELD EXPERIMENT DESIGN

*In situ* chemical oxidation involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming contaminants present in groundwater, soil, and bedrock into less harmful chemical species (United States Environmental Protection Agency [USEPA], 2006). The focus of this field experiment is on the chemical oxidation of TCE and its daughter products 1,1-DCE, cis-1,2- DCE, trans-1,2-DCE, and VC present in the Chatsworth formation groundwater beneath the SSFL. The objective of the field experiment is to successfully deliver a chemical oxidant into the Chatsworth formation via the fracture network and to evaluate the effectiveness of the oxidant using a set of applicable performance criteria. The field experiment design involves determining the most suitable oxidant, selecting an appropriate test area, creating a set of performance criteria to evaluate the field experiment, outlining injection parameters including concentration, volume, flow rate, and test duration, and creating a monitoring plan to gather data for evaluating the performance criteria.

## 3.1 CHEMICAL OXIDANT SELECTION

There are a variety of types of oxidants with varying physical and chemical properties that have been successfully demonstrated using *in situ* chemical oxidation technology. For the purposes of this field experiment, four oxidants were evaluated to determine the most appropriate oxidant for the hydrogeologic setting and contaminant distribution at the selected field experiment location:

- Permanganate
- Persulfate
- Fenton's Chemistry
- Ozone

The oxidants were evaluated based on several characteristics including oxidation potential and the capacity to transform TCE and its daughter products, the ability to be distributed in the fracture network, persistence in the subsurface, and capacity for diffusion into the porous rock matrix. The oxidants were also evaluated on their potential to generate reaction byproducts and adverse effects that could limit success in regard to the performance criteria. Table 3-1 summarizes the physical and chemical characteristics of the oxidants.

The permanganate ion ($MnO_4^-$) is a strong oxidant capable of oxidizing chlorinated ethenes including TCE and its daughter products DCE and VC. It has slower reaction kinetics than

ozone and Fenton's reagent and has been shown to persist in the unlithified sediments for a period of months and potentially more than one year (USEPA, 2006). In the Chatsworth formation bedrock, application of excess permanganate creates a concentration gradient resulting in diffusion of $MnO_4^-$ into the rock matrix pore spaces where the majority of the contaminants reside. Based on these characteristics, permanganate was selected as the most appropriate oxidant for the field experiment.

$MnO_4^-$ can be combined with either the sodium ($Na^+$) or potassium ($K^+$) cation to form the permanganate salt which is dissolved in water to form the oxidant solution delivered to the subsurface. Stoichiometrically, the molar ratio of permanganate required for the transformation of TCE is the same for each salt. The primary difference between potassium and sodium permanganate is the cost and method of preparation for delivery to the subsurface. Potassium permanganate was selected as the oxidant for the field experiment due to cost efficiency. Sodium permanganate may alternately be used in the field experiment pending further review and evaluation.

One potential disadvantage of using permanganate as an oxidant is the potential for side reactions to occur that will result in the precipitation of manganese oxides during the reaction of permanganate with TCE, other chlorinated ethenes, naturally occurring reactive minerals, and organic carbon sources in the rock matrix. Preliminary evaluation of potential pyrite-permanganate reaction pathways indicate that permanganate will oxidize naturally occurring pyrite ($FeS_2$) in the subsurface resulting in the generation of manganese oxides such as pyrolusite ($\beta$-$MnO_2$) and possibly iron oxides. Although there are other possible reaction pathways, the general pathway described below shows the likelihood of permanganate to react with pyrite in the subsurface environment.

$$FeS_2 + MnO_4^- + 4H_2O \Leftrightarrow \beta\text{-}MnO_{2(s)} + Fe(OH)_{2(s)} + SO_4^{2-} + S^{2-} + 6H^+ + 3e^-, \text{ Log K= 9.66}$$

The reaction suggests that for every mole of pyrite oxidized by permanganate, one mole of pyrolusite may be generated. The precipitation of manganese and possibly iron oxides on fracture network and rock matrix pore surfaces could lead to reduced permeability in fractures and pores thus limiting advective and diffusive mass transport of the oxidant. Precipitation of manganese and iron oxides also has the potential to coat reactive surfaces within the pores thus limiting the amount of surface area available for reactions with adsorbed contaminants. The impact of manganese and iron oxide precipitation and deposition on rock matrix pore surfaces

will be assessed using laboratory bench tests and through rock core analysis during the field experiment.

## 3.2 TCE-PERMANGANATE OXIDATION REACTIONS

In an aqueous solution, $KMnO_4$ disassociates into $K^+$ and $MnO_4^-$. Under normal subsurface pH and temperature conditions, the carbon-carbon double bond is broken and the ethenes are eventually converted to carbon dioxide and water through hydrolysis via additional oxidative steps by the permanganate ion (Yin, et. al, 1999).

At a pH between 3.5 and 12, complete oxidation of one mole of TCE requires two moles of $KMnO_4$ and the transfer of six electrons according to the following reaction:

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^-$$

Oxidation reactions for the resulting daughter products DCE and VC are shown below:

$$\text{DCE:} \quad 8KMnO_4 + 3C_2H_2Cl_2 \rightarrow 6CO_2 + 8MnO_2 + 8K^+ + 2OH^- + 6Cl^- + 2H_2O$$

and,

$$\text{VC:} \quad 10KMnO_4 + 3C_2H_3Cl \rightarrow 6CO_2 + 10MnO_2 + 10K^+ + 7OH^- + 3Cl^- + H_2O$$

The complete oxidation of chlorinated ethenes results in $K^+$ and chloride ($Cl^-$) ions, carbon dioxide ($CO_2$) and water ($H_2O$), manganese oxides, and potentially iron oxides. $CO_2$ is naturally present in the subsurface due to biological activity and manganese and iron oxides are naturally occurring minerals, and therefore are not anticipated to lead to groundwater quality issues.

## 3.3 PERFORMANCE CRITERIA

A set of performance criteria was selected to assess the effectiveness of *in situ* chemical oxidation in a fractured sandstone bedrock setting. The criteria include: evaluating oxidant delivery and distribution; the extent and magnitude of TCE oxidation; the oxidant loading required to overcome natural oxidative demand in the Chatsworth formation; and the evaluation of potential mineral precipitation and deposition within the rock matrix pores due to reaction of the oxidant with constituents on pore surfaces. Performance criteria will be evaluated through

bench scale testing and through a monitoring plan that will include groundwater and rock core sampling and analysis.

A primary objective of the test is to evaluate the ability to deliver an oxidant into two distinct geological matrices (i.e., fracture network and rock matrix pores) within the Chatsworth formation. Because the two geological matrices have hydraulic conductivities that differ by orders of magnitude, the field experiment will evaluate the ability of the fracture network to accept the volume of oxidant required to react with TCE in subsurface and determine the lateral and vertical distribution of oxidant within the fracture network. The field experiment will also evaluate the capacity of the oxidant to diffuse into the rock matrix where the majority of TCE resides. Distribution will be assessed using a monitoring well network to measure oxidant concentrations at varying lateral and vertical distances from the injection point over time. Rock core samples will be obtained during the test from up to two locations near the injection point and analyzed to evaluate potential oxidant diffusion into the rock matrix.

The field experiment will assess the extent of oxidation of aqueous TCE in the fracture network and rock matrix pore water, and TCE sorbed to organic carbon sources in the rock matrix. TCE concentrations will be measured over time by collecting and analyzing groundwater samples from varying lateral and vertical distances from the injection point. Rock core samples will be analyzed to evaluate the potential of TCE to be oxidized within the rock matrix. Baseline groundwater, rock matrix pore water, and sorbed TCE concentrations will be compared against analytical results obtained from the field experiment to assess TCE reactivity and destruction during the test.

A bench scale test will be conducted to assess the NOD of organic carbon sources and reactive minerals present in the Chatsworth formation. A large NOD can result in significant depletion of the injected oxidant, thus limiting the amount of oxidant available for reaction with the targeted contaminants. Once the NOD has been quantified, the required oxidant loading and injection concentration will be adjusted in order to deliver sufficient oxidant to the subsurface. Work plans describing this bench scale test are currently being developed.

The field experiment will also assess the impacts of TCE oxidation in the rock matrix pores from side reactions involving the potential precipitation of manganese oxides and possibly iron oxides on surfaces of the rock matrix pores. Rock core samples will be analyzed to determine the composition and magnitude of mineral formation and the extent of deposition on surfaces in the rock matrix pores.

## 3.4 CHEMICAL OXIDATION BENCH TEST

A bench scale test will be conducted concurrent with the chemical oxidant injection for the field experiment. The purpose of the bench test is to determine the NOD of Chatsworth formation groundwater and rock matrix, assess the magnitude of mineral deposits on the solid surfaces of the rock matrix associated with the oxidation reaction, evaluate the potential for manganese and iron oxide precipitation due to the oxidation reaction, and determine the oxidant loading required for subsurface delivery.

A work plan for the bench scale test is being prepared to guide the bench test. Following the bench scale test, a report will be prepared summarizing the findings and conclusions of the bench test such that the information can be used to further evaluate the design and/or effects of the field experiment.

## 3.5 INJECTION PARAMETERS

The design of the field experiment injection parameters focused on sustaining the injected oxidant concentration in the fractures within an estimated treatment zone to maximize the concentration gradient and oxidant diffusion into the rock matrix pore space. Remediation grade $KMnO_4$ will be mixed on site and delivered to the subsurface via a single injection well during pulsed injection events using gravity to generate the head required for delivery of the oxidant to the subsurface.

Depth to water in the proposed injection well location RD-35A was measure at 91 feet in February 2009. The injection well will have an open borehole interval which begins below the existing groundwater surface elevation in order to direct the injected oxidant solution into the saturated zone and minimize flow to the unsaturated zone. The open borehole interval will extend from approximately 100 feet to 150 feet bgs. A mixing tank located at ground level would result in 91 feet of head available for injection, equivalent to an injection pressure of 39 pounds per square inch. If the pressure head available due to gravity is not sufficient for the required oxidant delivery during the field experiment, mechanical pressure may be used to generate the desired injection pressure.

Pumping tests were performed in RD-35A and RD-35B in February 1998 (Sterling, 1999). In RD-35A, pumping was performed at 1 to 3 gallons per minute (gpm) for four hours with a total of 20 feet of drawdown observed in the well. Sustained pumping rates in RD-35B indicated the

lowermost zones in the well, from 334.5 feet to 350.5 feet bgs, had the lowest sustainable pumping rates and the uppermost zone, from 189.5 feet to 208 feet bgs, had the highest sustainable pumping rate. In February 2002, another pumping test was performed in RD-35B (MWH, 2004). Pumping was performed at 1.1 gpm for nine days and resulted in 150 feet of drawdown in the well. Based on pump test data, an injection flow rate of 1.5 gpm will be used for design calculations in this field experiment. The injection flow rate may vary or be adjusted throughout the test based on actual field conditions and evaluation of performance monitoring results.

$KMnO_4$ has an aqueous solubility of 60 grams per liter (g/L) at 20 $^oC$ (Reidies, 2009). However, dissolved concentrations are generally less in field applications due to ambient temperature and minerals present in supply water used to mix the injection solution. The design injection concentration for the field experiment is 20 g/L. The injection concentration is estimated to satisfy the total oxidant demand of the subsurface treatment area which is comprised of the NOD of the groundwater, pore water, and rock matrix and the chemical oxidant demand of TCE and associated VOCs. The design injection concentration may be modified based on results from the pre-injection bench test where the total oxidant demand could be calculated.

The field experiment will consist of 10 pulsed injection events for a duration of approximately one year. Each event will consist of 8 hours of injection per day for 5 days. A period of 25 days between injection events is planned to allow the oxidant to diffuse into the rock matrix. A design injection concentration of 20 g/L at an estimated flow rate of 1.5 gpm would result in an injection volume of 720 gallons per day and an injected mass of 120 pounds of $KMnO_4$ per day. At the end of each day, the injection well will be filled and allowed to deliver oxidant over night. The 10-inch diameter injection well has a storage capacity of 370 gallons available for additional oxidant to be injected overnight. The resulting daily injection volume would be 1090 gallons per day for a total of 5,450 gallons for each injection event. After 10 events, a total of 54,500 gallons of solution and 9,000 pounds of $KMnO_4$ will have been injected into the subsurface.

The total injection duration and length, injection parameters, and frequency of injection events may be adjusted based on observed field conditions, injection system parameters, and performance monitoring data.

## 3.6 INJECTION SYSTEM EQUIPMENT

Major components of the field experiment injection system will include:

- A $KMnO_4$ mixing and storage tank with electric mixer,
- A recirculation pump for the mixing and storage tank,
- Secondary containment for the mixing and storage tank,
- Make-up water supply and injection transfer hoses, and
- Miscellaneous instrumentation for measuring injection flow rate, pressure, and total volume.

The mixing and storage tank should have a minimum capacity of 1,500 gallons to support planned mixing operations. The mixing tank will be equipped with an electric mixer operating continuously to maintain dissolution of $KMnO_4$. A recirculation pump will circulate the injection solution to aid in maintaining dissolution. The injection system will be equipped with a totalizer for measuring the total volume of oxidant solution injected and a flowmeter for monitoring injection flow rate. The injection solution will be run through a static mixer and bag filter prior to injection into the subsurface to prevent any solid $KMnO_4$ which may have precipitated out of solution from being injected into the well.

Secondary containment will be constructed around the mixing and storage tank and injection well so that any leak or release from the tank, piping, transfer hose or at the injection well head will be contained. Using a safety factor of 1.25 times the design storage volume of 1,500 gallons, the secondary containment will have a capacity 1,875 gallons. The secondary containment should be constructed of a high-density polyethylene liner (or equivalent) of a thickness that will adequately withstand normal wear and tear associated with mixing operations and environmental exposure for one year.

## 3.7 PERFORMANCE MONITORING

The purpose of the monitoring plan is to provide a basis for evaluating the field experiment effectiveness with respect to the performance criteria. Monitoring will consist of measuring and recording injection system parameters, groundwater quality parameters and contaminant concentrations in the fracture system surrounding the injection area, and collecting rock core samples for evaluating the oxidant effects and contaminant concentrations in the rock matrix.

Below is a summary of the performance criteria and corresponding monitoring that will provide data for the evaluation of the performance criteria:

| ***In Situ* Chemical Oxidation Field Experiment Performance Criteria** | **Monitoring for Assessment of Performance Criteria** |
|---|---|
| 1. Evaluate the delivery and distribution of the oxidant in the fractured sandstones of the Chatsworth formation. | Monitor groundwater quality parameters in surrounding wells including:<br>• visual observation of color,<br>• permanganate concentration,<br>• oxidation-reduction potential (ORP),<br>• pH,<br>• specific conductivity, and<br>• temperature.<br><br>Collect groundwater samples for laboratory analysis to evaluate vertical and lateral extent of oxidation in the fractures and analyze for:<br>• VOCs, and<br>• dissolved metals. |
| 2. Assess the extent of oxidation of TCE (and its daughter products) in the rock matrix. | Collect rock core samples to evaluate diffusion into rock matrix and oxidation of TCE. Perform visual observation of color in rock core and distance from nearest fracture. Sample and analyze for VOCs at various distances from fractures in the rock core. Convert TCE and daughter products into pore water concentrations and compare against baseline pore water concentrations. |
| 3. Evaluate the magnitude of contaminant concentration reduction in the rock matrix. | Collect rock core samples to evaluate total mass of TCE and daughter products removed from rock matrix. Convert target VOCs into pore water concentrations and compare against baseline pore water concentrations. |
| 4. Assess the natural oxidant demand of the minerals and/or organics present in the rock matrix. | Collect rock core and perform bench test to measure oxidant consumption by rock matrix. |
| 5. Assess the magnitude and extent of mineral deposits on the solid surfaces of the rock associated with the oxidation reaction. | Collect rock core samples and use Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM/EDS) technologies to observe extent of mineral deposition on pore space surfaces. |

| *In Situ* Chemical Oxidation Field Experiment Performance Criteria | Monitoring for Assessment of Performance Criteria |
|---|---|
| 6. Assess the occurrence and effects of the precipitation of oxidation reaction by-products in the fracture system. | Monitor injection pressure and flow rate during field experiment to assess changes in hydraulic conductivity due to injection.<br>Conduct a short-term hydraulic test following re-drilling of RD-35A and at the conclusion of the injection to measure permeability variation. |

### 3.7.1 Injection System

Injection system parameters will be monitored on a weekly basis to assess the delivery of the oxidant and include:

- Injection flow rate,
- Injection pressure,
- Injection $KMnO_4$ concentration, and
- Total volume injected.

For each batch of $KMnO_4$ solution that is prepared, the volume of make-up water, the mass of $KMnO_4$, and the batch number will be recorded.

### 3.7.2 Groundwater

A monitoring well network surrounding injection well RD-35A will be used to monitor groundwater quality parameters and contaminant concentrations. The monitoring well network consists of wells located within a radius that oxidant could potentially be observed during the field experiment and includes C-1, C-10, RD-31, RD-35B, RD-35C, RD-37, RD-72, RD-73, WS-14, HAR-24, and HAR-25. The wells have an open borehole or casings that are screened in either the same vertical interval or deeper vertical intervals as the injection well. Two wells, RD-31 and RD-35C, have Westbay multi-level sampling systems installed which allow monitoring at 10 and 12 discrete vertical intervals, respectively. FLUTe liners will be constructed of materials compatible with $KMNO_4$ and be installed in coreholes C-1 and C-10. The conceptual layout of the monitoring ports includes alternating open/closed intervals with 10-foot spacing to an approximate depth of 250 feet bgs, although alternate designs may be

considered that target fracture zones. Final design of these multi-level systems will be conducted in consultation with DTSC. Data from wells will be used to evaluate groundwater quality parameters and contaminant concentrations in the lateral and vertical directions.

Two additional monitoring wells will be installed at distances of approximately 50 feet and 100 feet northeast of injection well RD-35A and be completed to a target depth of about 250 feet bgs. FLUTe liners will be installed at these locations similar to that specified above for coreholes C-1 and C-10. Existing and proposed monitoring well locations are shown in plan view on Figure 2-2.

The distribution of oxidant in the fracture network will be evaluated by monitoring groundwater quality parameters in wells surrounding injection well RD-35A. The groundwater quality parameters include $MnO_4^-$, ORP, visual observation of color, pH, temperature, and specific conductivity. When $KMnO_4$ is injected into groundwater, it disassociates into $K^+$ and $MnO_4^-$. Due to the reaction of $MnO_4^-$ with constituents in the groundwater and the rock matrix, $K^+$, which leads to a rise in the specific conductivity, is expected to be observed ahead of the oxidant reaction front and will serve as an indicator of the impending arrival of the oxidant. $MnO_4^-$, ORP, and color are direct indicators of the presence of the oxidant and will be monitored to observe the arrival and persistence of the oxidant in the field experiment test area.

Groundwater samples will also be collected from surrounding monitoring wells and sent to a laboratory to be analyzed for VOCs. Increasing concentrations of dissolved metals during *in situ* chemical oxidation has been reported in some field applications due to mobilization of some metals which can occur under increasing oxidizing conditions. Natural attenuation of these dissolved metals is generally achieved within acceptable transport distances and time frames as subsurface conditions return to pre-injection levels (USEPA, 2006). In addition to VOCs, groundwater samples will be analyzed for dissolved metals to evaluate metals mobilization resulting from the field experiment.

Samples will be collected from the monitoring well network before injection begins to establish baseline groundwater quality parameters and contaminant concentrations. Once injection activities begin, groundwater quality parameters will be monitored on a weekly basis and groundwater samples will be collected for laboratory analysis on a quarterly basis in wells nearest to the injection well, including RD-35B, RD-35C and the two new proposed monitoring wells.

Additional wells in the monitoring well network may be selected and added to the monitoring schedule in order to maintain a dynamic response in monitoring during the field experiment. As groundwater quality parameters change or the arrival of permanganate is observed in monitoring wells, additional wells will be monitored based on their location and evaluation of the distribution of the oxidant.

Post-injection monitoring will be conducted in all wells that were monitored and sampled during the field experiment. Groundwater quality parameters will be monitored on a weekly basis and groundwater samples will be collected for laboratory analysis on a quarterly basis for two quarters following the conclusion of injection activities.

### 3.7.3 Rock Matrix

Up to two coreholes will be drilled approximately one year after initiating oxidant injection to evaluate the extent of oxidation and magnitude of reduction of TCE and its daughter products in the rock matrix surrounding the injection area.

The rock cores will be logged and visual observations performed to evaluate potential permanganate diffusion at fracture locations. Samples from individual rock cores will be collected at every foot below ground surface in rock core that is not visibly impacted by permanganate. Where visible permanganate impact is observed, fractures will be identified, and samples will be collected in each vertical direction from the fracture. Samples obtained from individual rock cores will be crushed and analyzed for select VOCs and possibly mineralogy using methods outlined in Appendix C of the Phase 2 Northeast Area Chatsworth Formation Work Plan (MWH, 2005). A limited number of rock core samples where permanganate has visibly penetrated the rock matrix will also be analyzed using a combination of SEM/EDS technologies to evaluate potential manganese and iron oxide precipitation and coating of fracture and pore surfaces.

# 4.0 HEALTH AND SAFTEY

$KMnO_4$ is a strong oxidizer and must be handled appropriately. A material safety data sheet for potassium permanganate is included as Attachment A. The oxidizer will be delivered to the site on pallets in approved 55-pound pails that comply with California Department of Transportation regulations. The oxidizer will be stored indoors in a secure location until required for mixing and injection. The containers of $KMnO_4$ will only be opened within a secondary containment structure. All personnel within the secondary containment will wear personal protective equipment (PPE) consisting of a chemical splash suit (Tyvek or equivalent), face shield, safety goggles, hard hat, and chemical resistant gloves and boots. Personnel responsible for opening $KMnO_4$ containers and mixing injection solutions will wear a half mask or full face respirator with organic vapor respirator cartridges in addition to the required PPE.

In addition to the existing SSFL Site Health and Safety Plan (HASP) (MWH, 2003), a HASP will be developed specifically for tasks associated with the field experiment. The procedures described in the HASP will be implemented and enforced by a site safety officer who will be present during site work. The purpose of the HASP will be to:

- Assign personnel with health and safety responsibilities;
- Establish process safety requirements for all equipment, including hazards associated with the operation of motorized equipment;
- Prescribe mandatory operating procedures; and
- Establish emergency response procedures including a solid and liquid potassium permanganate spill contingency plan.

Prior to initiating any site work, all field personnel will receive training on proper $KMnO_4$ handling, storage, and injection procedures. Site-specific health and safety procedures will be presented during daily safety tailgate meetings.

# 5.0 PERMITTING

An application for a General Waste Discharge Requirements (WDR) for Groundwater Remediation at Petroleum Hydrocarbon Fuel and/or Volatile Organic Compound Impacted Sites (Order No. R4-2005-0030) will be submitted to the Los Angeles Regional Water Quality Control Board (LARWQCB). This General WDR covers the remediation of groundwater via *in situ* chemical oxidation using $KMnO_4$ as the oxidant and includes demonstration studies (i.e., field experiments) prior to the implementation of full scale remediation projects.

In addition, a Hazardous Materials Permit will be obtained from the Ventura County Fire Protection District (VCFPD) for the storage, handling, and use of $KMnO_4$ during the field experiment. $KMnO_4$ is Class 2 oxidizer and will be stored, handled, and used in accordance with all requirements of the Uniform Fire Code.

## 6.0 FIELD EXPERIMENT REPORTING

Results of the field experiment will be summarized at the conclusion of injection activities and the last round of post-injection monitoring. All activities associated with the field experiment including bench test results, field experiment modifications, and additional monitoring well installation will be documented. Injection flow rates, total volume and total mass injected, and sampling and analytical results obtained during performance monitoring will also be included. The results and summary of the field experiment and discussion of the feasibility of *in situ* chemical oxidation as a groundwater remediation technology at the SSFL will be incorporated into the feasibility study and submitted to DTSC and summarized in the feasibility study report.

## 7.0 IMPLEMENTATION SCHEDULE

The following is a list of major milestones and dates for the field experiment.

| ***Task*** | ***Targeted Completion Date*** |
|---|---|
| Infrastructure and permitting | January 2010 |
| Operations | January 2011 |
| Post-test sampling | April 2011 |
| Performance reporting | July 2011 |

## 8.0 REFERENCES

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# TABLES

## Table 3-1
## Summary of Characteristics Considered in Chemical Oxidant Selection

| Oxidant | Reactive Species | Oxidizing Strength ($E_h$) | Contaminants Amenible to Oxidation | Delivery Form | Solubility @ 1 atm, 25 °C | Subsurface Persistence | Stoichiometric Molar Consumption Ratio[1] | Cost | Undesirable Reaction Byproducts | Technology Development in Fractured Rock Setting | Safety Considerations | Comments |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Potassium Permanganate | $MnO_4^-$ | 1.7 V | chlorinate ethenes, aromatics, PAHs, phenols, energetics, pesticides | powder/ liquid | 60 g/L | >3 months | 2:1 | $1.80/lb | manganese and iron oxide precipitation | Moderate body of technical literature and documented field experiments. | - chemical resistant clothing, respirator, eye protection required for mixing and injection<br>- contact with oxidizable substances can cause violent reaction<br>- potential for airborne spreading of permanganate crystals during mixing due to wind | - Favorable persistence in subsurface<br>- Density-driven vertical transport due to specific gravity > 1<br>- Existing documented field studies and technical literature<br>- Manganese and iron oxide precipitation may reduce fracture and matrix permeability and limit advective transport and diffusive mass transfer<br>- Relatively safe to handle<br>- Most cost efficient |
| Sodium Permanganate | $MnO_4^-$ | 1.7 V | chlorinate ethenes, aromatics, PAHs, phenols, energetics, pesticides | liquid | 400 g/L | >3 months | 2:1 | $6.50/lb | manganese and iron oxide precipitation | Moderate body of technical literature and documented field experiments. | - chemical resistant clothing, eye protection required for injection<br>- contact with oxidizable substances can cause violent reaction | - Higher solubility compared to potassium permangate results in greater vertical distribution due to density-driven transport and increased diffusion into the rock matrix<br>- Higher solubility potentially results in greater manganese and iron oxide precipitation<br>- Delivery as liquid eliminates need for mixing<br>- Expensive compared to potassium permanganate |
| Sodium Persulfate | $SO_4^{2-}$ | 2.1 V | chlorinated ethenes, petroleum hydrocarbons, BTEX, PAHs, phenols, energetics | powder/ liquid | 730 g/L | weeks - months | 5.4:1 | $1.20/lb | -- | Limited technical literature and documented field experience in bedrock setting. | - chemical resistant clothing, eye protection required for injection<br>- contact with oxidizable substances can cause violent reaction | - Increased density-driven and diffusive transport due to high injection concentration<br>- Persulfate ion is not significantly invovled in sorption reactions, and may not react as readily as permanganate with aquifer organic matter<br>- Less stable than permanganate<br>- No undesirable reaction bioproducts<br>- Emerging technology, less information available regarding fundamental chemistry and reactions in subsurface<br>- Requires bench testing to confirm capacity to oxidize TCE |
| Activated Persulfate | $SO_4^{2-}$, $\cdot SO_4^{2-}$ | 2.1 V (persulfate)<br>2.6 V (sulfate radical) | chlorinated ethenes, chlorinated ethanes, petroleum hydrocarbons, BTEX, PAHs, phenols, pesticides, energetics | powder/ liquid | 730 g/L | hours - weeks | 1:1 | $1.20/lb plus activator | potential for metal precipitation with iron activator | Limited technical literature and documented field experience in bedrock setting. | - chemical resistant clothing, eye protection required for injection<br>- contact with oxidizable substances can cause violent reaction | - Activator chemistry adds complexity to injection<br>- Activators speed up reaction kinetics and limit subsurface contact time and distribution<br>- Maximum contaminant transformation obtained when activator and persulfate are initially contacted in subsurface due to fast reaction rate |
| Fenton's Chemistry (hydrogen peroxide and Fe(II)) | $\cdot HO_2$, $H_2O_2$, $\cdot OH$, | 1.7 V (perhydroxyl radical)<br>1.8 V (hydrogen peroxide)<br>2.8 V (hydroxyl radical) | chlorinated ethenes, chlorinated ethanes, petroleum hydrocarbons, BTEX, PAHs, phenols, energetics | liquid | Potential Injection Concentrations: 5-10% $H_2O_2$ solution and between 4:1 and 8:1 molar ratio of $H_2O_2$ to Fe(II)[2] | minutes - hours | 1:1 - 2:1 | N/A | colloidal iron particle precipitation, excessive heat and oxygen gas generation | Limited technical literature and documented field experience in bedrock setting. | - Explosion potential due to large volume of gas generation<br>- Burn potential due to highly exothermic reaction | - Fast reaction rate limits oxidant transport<br>- $O_2$ gas generation may lead to entrapped air in the fractures and rock matrix pore space and reduction of hydraulic conductivity<br>- Precipitation of Fe(III) could result in permeability reduction in the rock matrix<br>- Complex reaction chemistry makes treatment design and analysis difficult |
| Ozone | $O_3$ | 2.1 V | chlorinated ethenes, some chlorinated ethanes, petroleum hydrocarbons, BTEX, PAHs, phenols, pesticides, energetics | gas | 6.4 mg/L[3] | minutes - hours | 3:2 | N/A | fugitive vapors containing partially reacted contaminants | Limited technical literature and documented field experience in bedrock setting. | - Inhalation hazard due to toxicity of ozone | - Dissolved aqueous ozone decomposes more rapidly than gaseous<br>- Low aqueous solubility<br>- Fast decomposition limits advective transport and diffusion into the rock matrix<br>- Ozone injection usually coupled with soil vapor extraction to prevent escape of fugitive vapors |

**Notes:**
1. Molar consumption rate based on reaction of oxidant with TCE.
2. Injection concentrations vary and are dependent on soil geochemistry.
3. Solubility of 1.5% ozone by weight in air at 20 °C.

**Acronyms:**

BTEX - benzene, toluene, ethylbenzene, xylenes
Fe - iron
g/L - grams per liter
$H_2O_2$ - hydrogen peroxide
$\cdot HO_2$ - perhydroxyl radical
lb - pound
mg/L - milligrams per liter
$MnO_4^-$ - permanganate ion
$\cdot OH$ - hydroxyl radical
$O_3$ - ozone
PAH - polynuclear aromatic hydrocarbon
$SO_4^{2-}$ - sulfate
$\cdot SO_4^{2-}$ - sulfate radical
V - volt

**Sources:**
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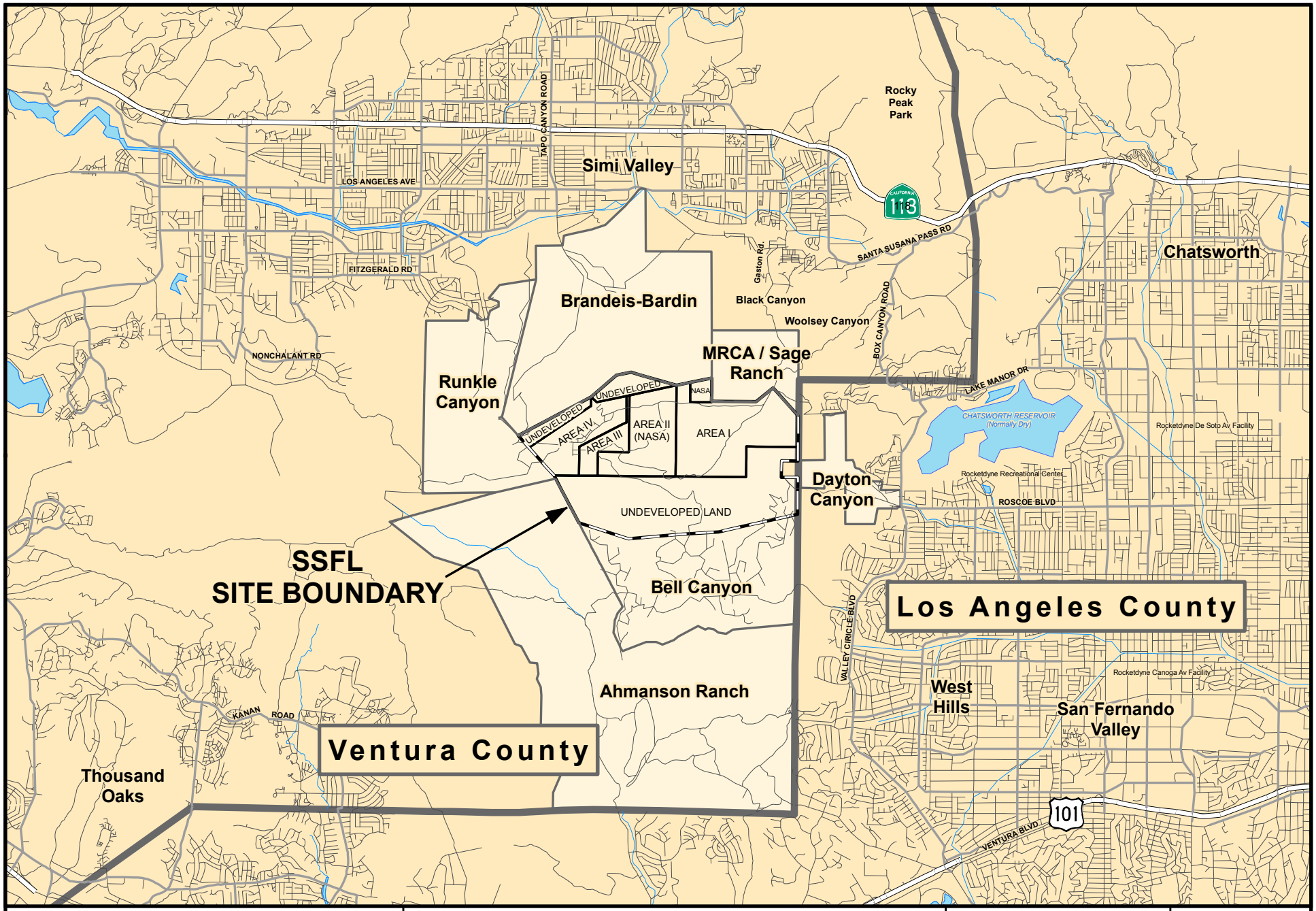
# FIGURES




# SANTA SUSANA FIELD LABORATORY

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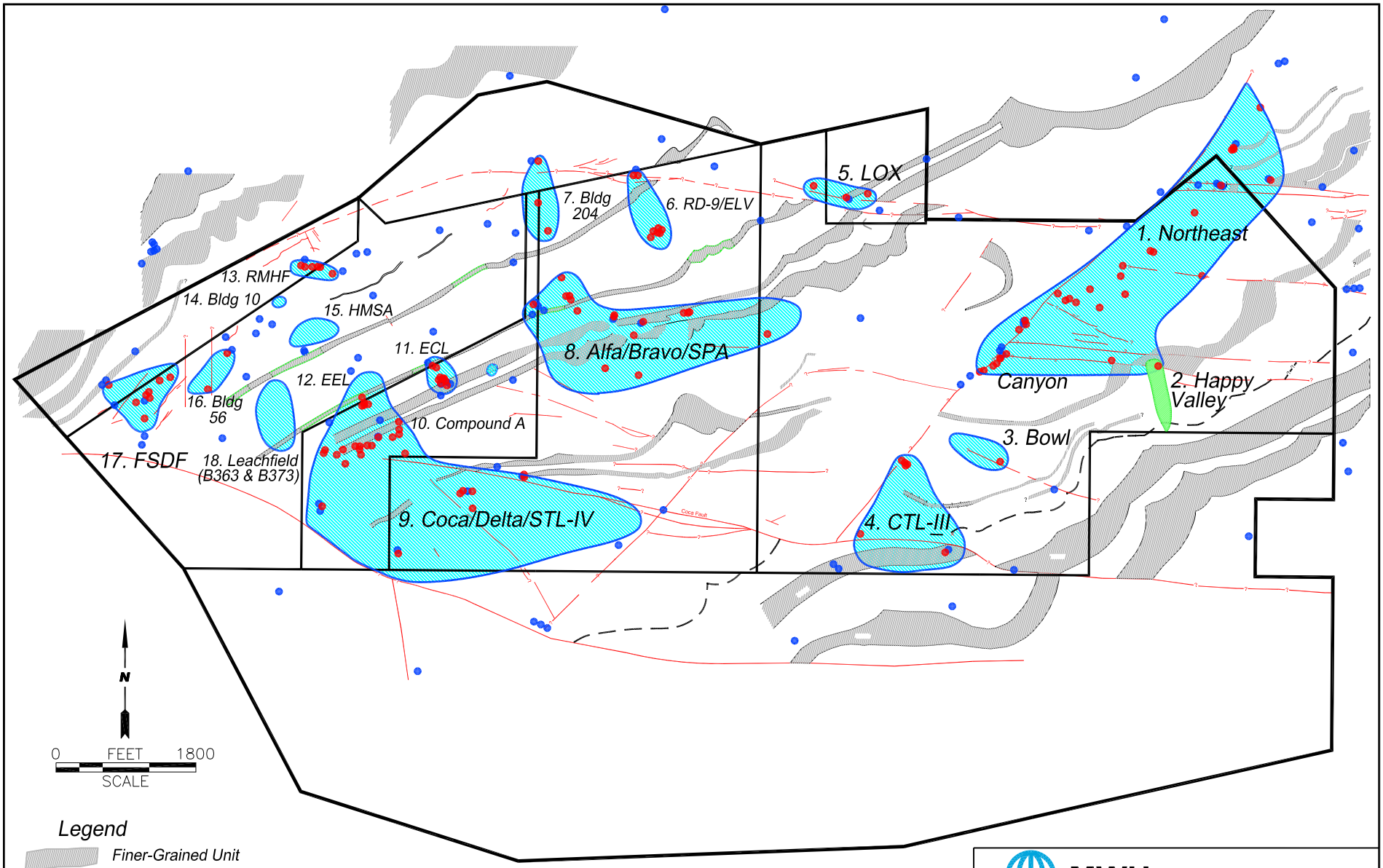
Date: Feb 04, 2009

## Regional Map

## FIGURE 1-1




The original version of theis figure includes colorized features and shading. A black and white copy of the figure should not be used because it may not accurately represent the information presented.

**MWH**

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VENTURA COUNTY, CALIFORNIA
MAY 2009

## AREAS OF IMPACTED GROUNDWATER AT THE SSFL

FIGURE 2-1

FILE: CAD MLUEBKE\BOEING\SANTA SUSANA\WORKPLAN FS 4 09\AREAS OF IMPACTED GW 4 16 09

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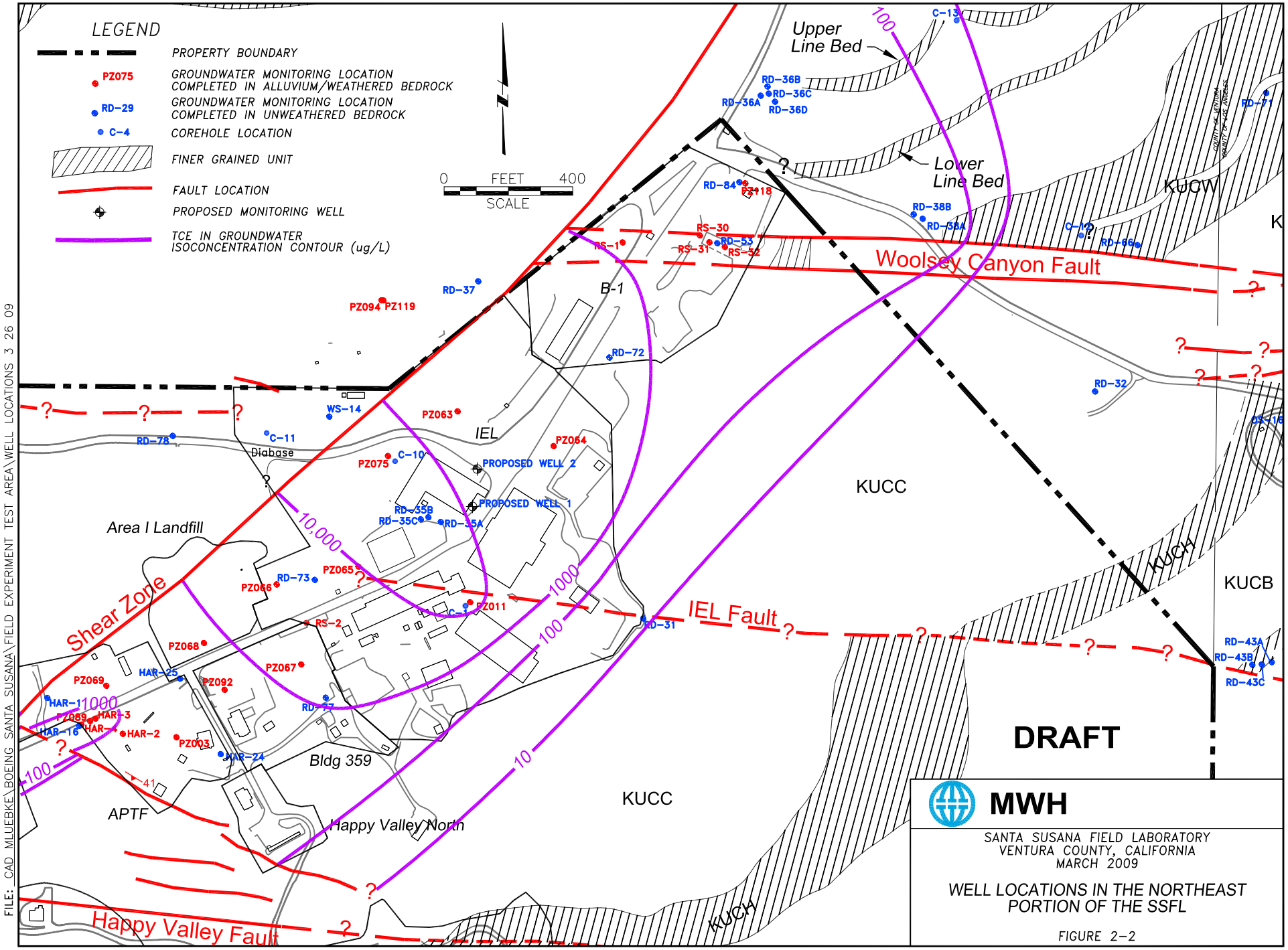
LEGEND
PROPERTY BOUNDARY
PZ075 GROUNDWATER MONITORING LOCATION COMPLETED IN ALLUVIUM/WEATHERED BEDROCK
RD-29 GROUNDWATER MONITORING LOCATION COMPLETED IN UNWEATHERED BEDROCK
C-4 COREHOLE LOCATION
FINER GRAINED UNIT
FAULT LOCATION
PROPOSED MONITORING WELL
TCE IN GROUNDWATER ISOCONCENTRATION CONTOUR (ug/L)
N
0 FEET 400
SCALE
Upper Line Bed
Lower Line Bed
Woolsey Canyon Fault
IEL Fault
Shear Zone
Happy Valley Fault
Area I Landfill
Bldg 359
APTF
Happy Valley North
Diabase
B-1
IEL
KUCC
KUCW
KUCH
KUCB
PROPOSED WELL 1
PROPOSED WELL 2
10,000
1000
100
10
41
DRAFT
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VENTURA COUNTY, CALIFORNIA
MARCH 2009
WELL LOCATIONS IN THE NORTHEAST PORTION OF THE SSFL
FIGURE 2-2
FILE: CAD MLUEBKE\BOEING SANTA SUSANA\FIELD EXPERIMENT TEST AREA\WELL LOCATIONS 3 26 09

Northwest

A

Southeast

A'

N36°W — BEND IN SECTION — S87°E

C-11 | WS-14 | Shear Zone | C-10 | RD-35C RD-35B RD-35A | C-1 | RD-31D

~1830' msl (Prior to C-1 Pumping Test)

~1550' msl

Sage Member

Canyon Member

Woolsey Member

Happy Valley Member

Bowl Member

Depth of 642'

Depth of ~703'

Depth of 600'

Depth of 542'

Depth of 750.5'

Depth of 850'

~75° Southeastward Dip to Shear Zone

Happy Valley Member

Bowl Member

Elevation (Feet msl)

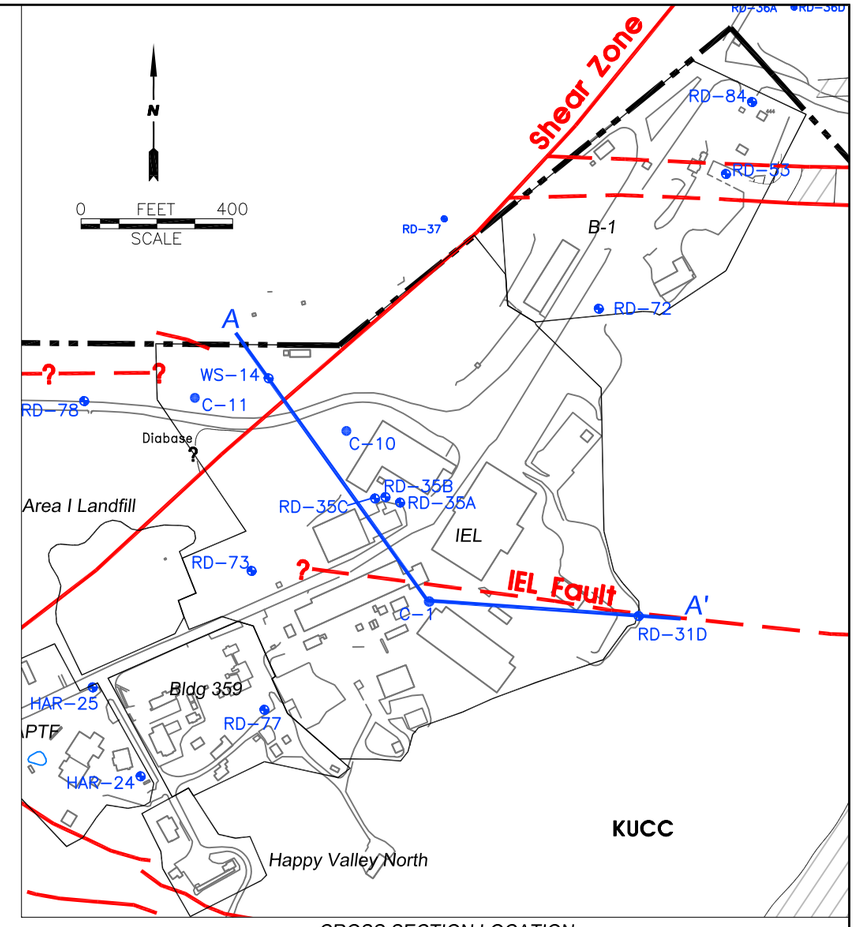
2000 1900 1700 1500 1300 1100 900 700

Legend

Estimated Water Table Elevation

0 FEET 200

SCALE




CROSS SECTION LOCATION

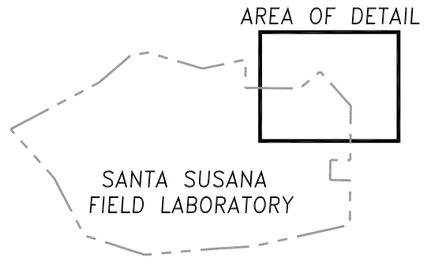
LEGEND

PROPERTY BOUNDARY

FINER GRAINED UNIT

FAULT LOCATION

RD-29 GROUNDWATER MONITORING LOCATION COMPLETED IN UNWEATHERED BEDROCK




**DRAFT**

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MARCH 2009

*CROSS SECTION OF THE FIELD EXPERIMENT TEST AREA*

FIGURE 2-3

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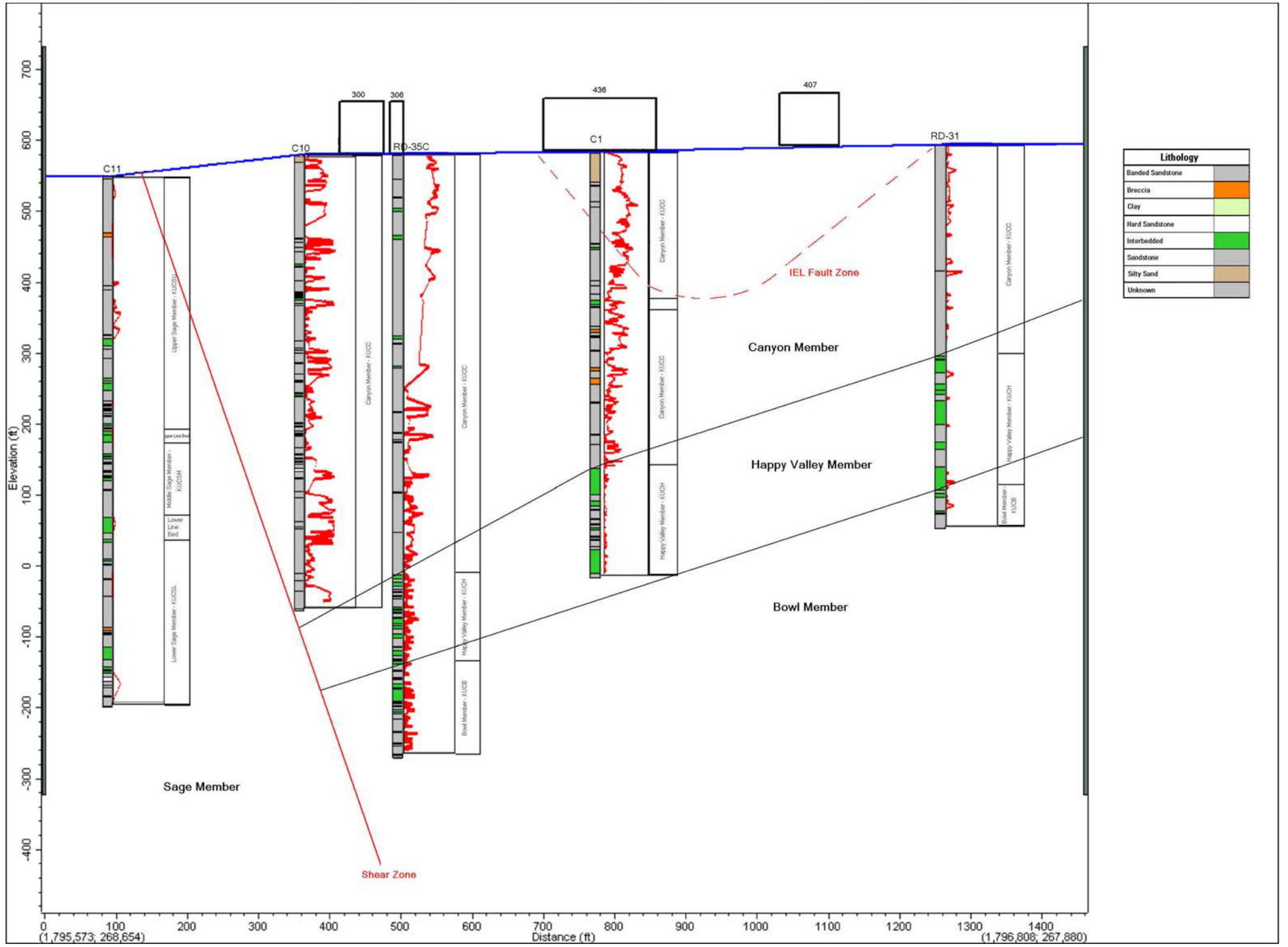


**Figure 2-4. Transect through the Instrument Equipment Lab (IEL) Area showing profiles of TCE versus depth.**

The logarithmic plot scale for each corehole was set to be the same, and ranged from 0 to 100,000 g/L porewater.

Source: Phase 2 Northeast Area Groundwater Characterization Technical Memorandum (Parker, et. al, 2008)

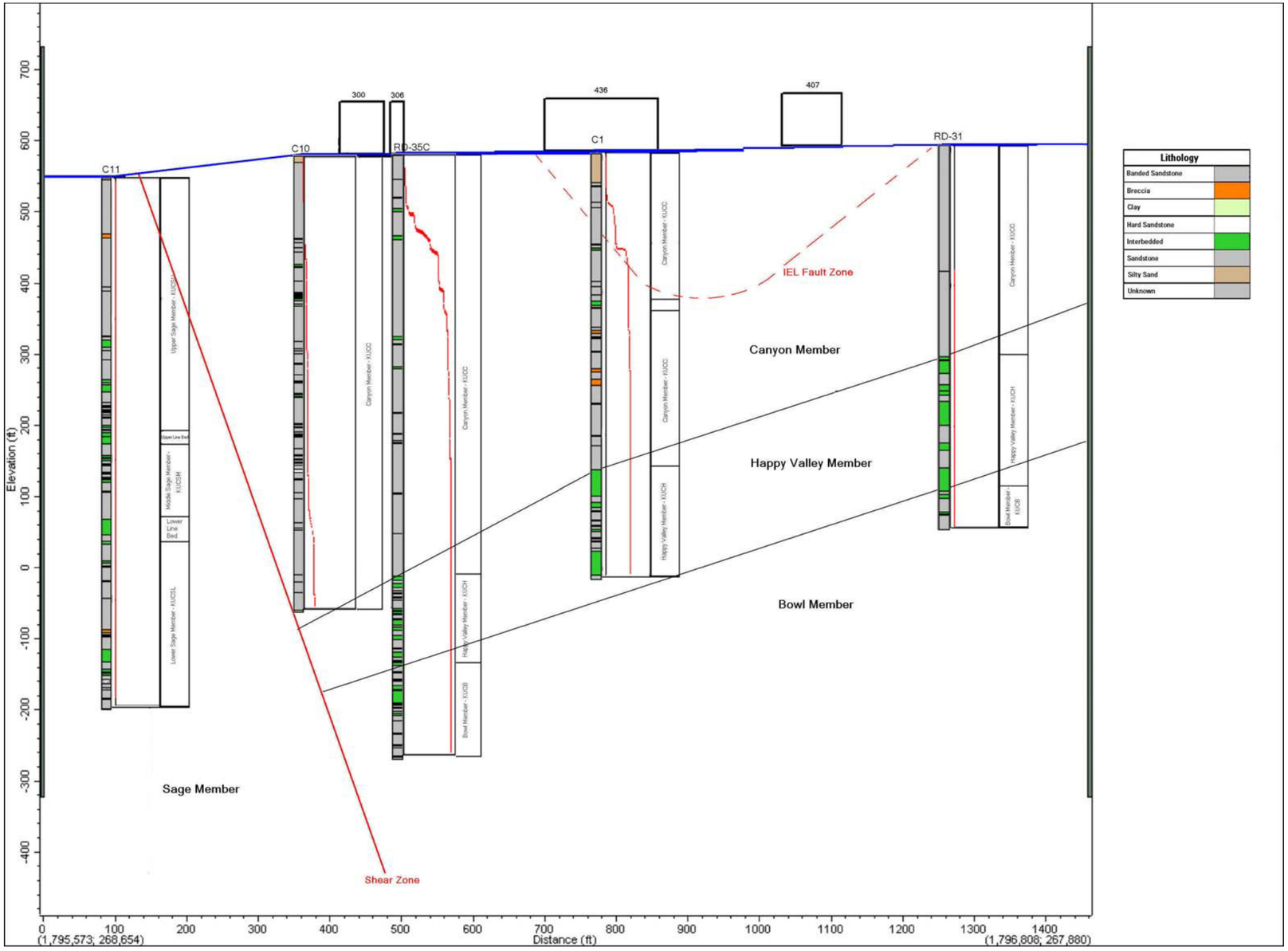


**Figure 2-5. Transect Through the Instrument Equipment Lab (IEL) Area Showing Cumulative Equivalent TCE Mass**

Masses were integrated by calculating mass values for each sample and assuming that these values remained constant for the depth range between the midpoint to the sample above and the midpoint to the sample below, and multiplying by the area to obtain mass on a horizontal per-meter-squared basis. Masses were then summed over the length of the corehole. Non-detect values were assumed to have concentrations of zero. The plot scale for each corehole was set to be the same, and ranged from 0 to 200g/$m^2$.

Source: Phase 2 Northeast Area Groundwater Characterization
Technical Memorandum (Parker, et. al, 2008)

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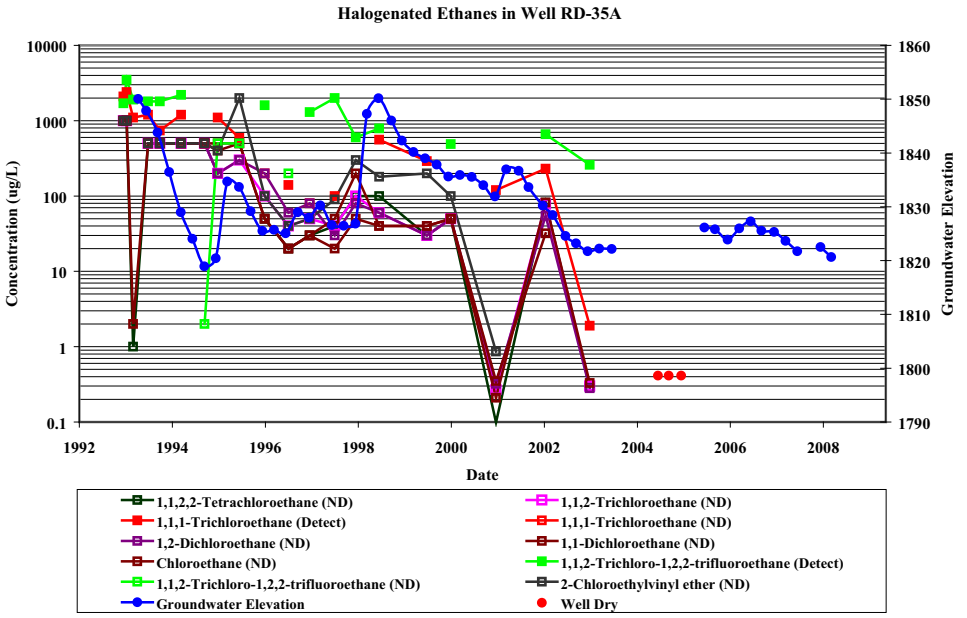


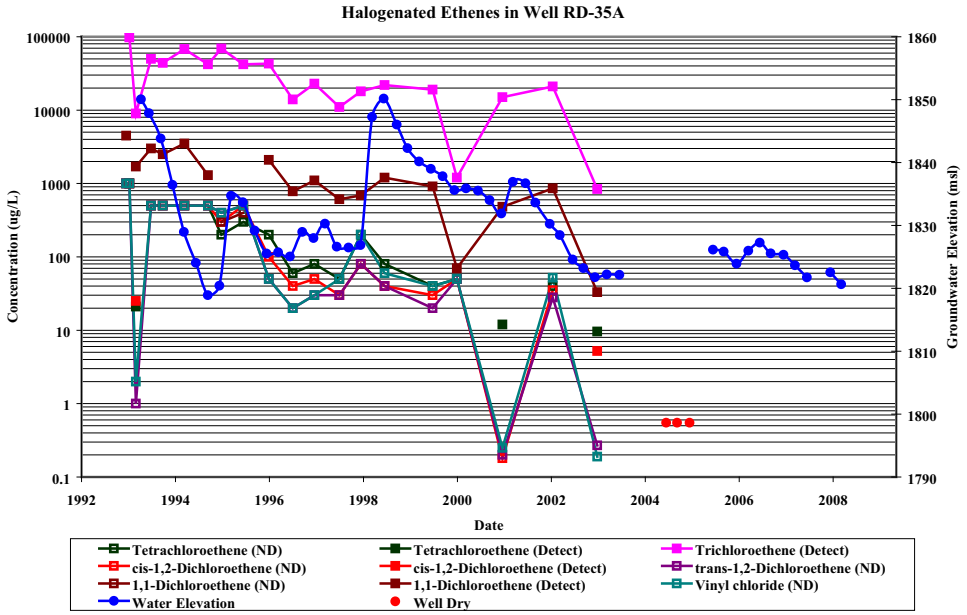


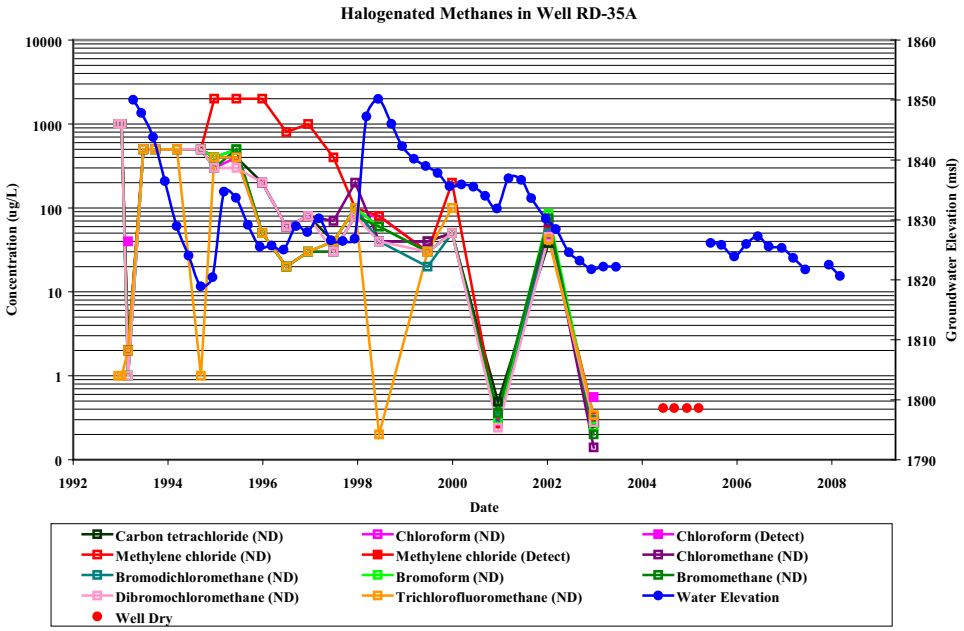


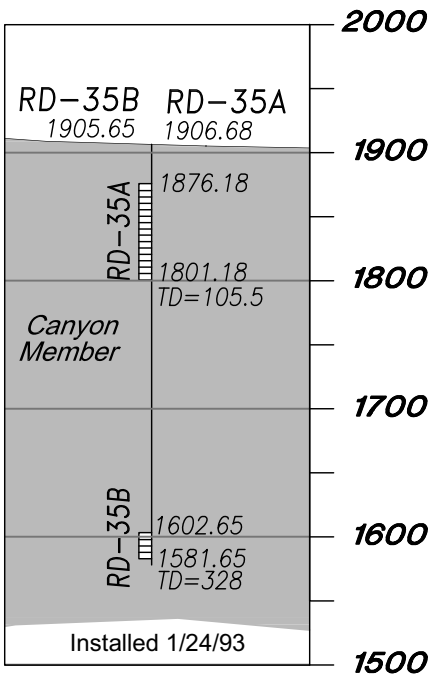


| Other Data: | Value | Units |
|---|---|---|
| 1,4-dioxane: | ND (Avg) | ug/L |
| Perchlorate: | ND | ug/L |
| Nitrate as $NO_3$: | 76 (Avg) | mg/L |
| Sulfate: | 235 (Avg) | mg/L |
| Chloride: | 135 (Avg) | mg/L |
| $^{18}O/^{2}H$: | -6.94/-43.06 | permil |
| $^{3}H$: | 8.81 ± 0.29 | TU |

**Notes:** NA-not analyzed ND-not detected
Avg - multiple results, average concentration
Tritium ($^{3}H$) sampled 8/93

MWH

SANTA SUSANA FIELD LABORATORY
VENTURA COUNTY, CALIFORNIA
Groundwater Elevations and
VOC Concentrations in RD-35A

Figure 2-6

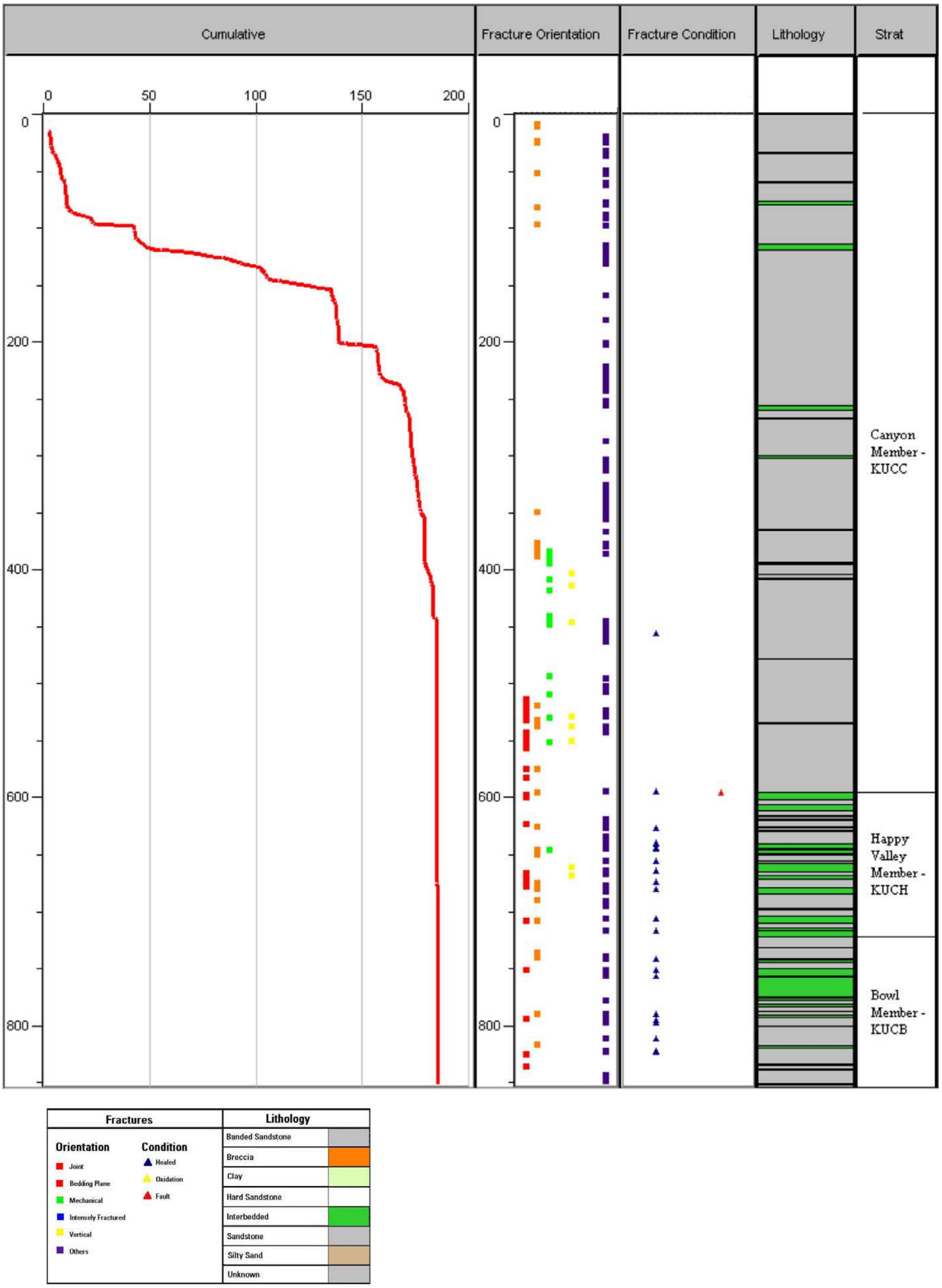


**Figure 2-7. RD-35C Cumulative Equivalent TCE Concentration Profile**

Masses were integrated by calculating mass values for each sample and assuming that these values remained constant for the depth range between the midpoint to the sample above and the midpoint to the sample below, and multiplying by the area to obtain mass on a horizontal per-meter-squared basis. Masses were then summed over the length of the corehole. Non-detect values were assumed to have concentrations of zero. Note: RD-35B from 0 - 359 ft, RD-35C from 359 - 853 ft

Source: Phase 2 Northeast Area Groundwater Characterization Technical Memorandum (Parker, et. al, 2008)

# ATTACHMENT A

# CAIROX®
# potassium permanganate

MATERIAL SAFETY DATA SHEET



## Section 1 Chemical Product and Company Identification

| | |
|---|---|
| **PRODUCT NAME:** CAIROX® potassium permanganate, $KMnO_4$ | |
| **TRADE NAME:** CAIROX® potassium permanganate | |
| **SYNONYMS:** Permanganic acid potassium salt<br>Chameleon mineral<br>Condy's crystals<br>Permanganate of potash | |
| **MANUFACTURER'S NAME:** CARUS CHEMICAL COMPANY | **TELEPHONE NUMBER FOR INFORMATION:** (815) 223-1500 |
| **MANUFACTURING FACILITY:** Carus Chemical Company<br>1500 Eighth Street<br>P. O. Box 1500<br>LaSalle, IL 61301 | **CHEMTREC TELEPHONE NO.** (800) 424-9300<br>**EMERGENCY TELEPHONE NO.** (800) 435-6856 |

## Section 2 Composition/Information on Ingredients

| Material or Component | CAS No. | % | Hazard Data |
|---|---|---|---|
| Potassium Permanganate | 7722-64-7 | 97% min. $KMnO_4$ | PEL-C 5mg Mn per cubic meter of air<br>TLV-TWA 0.2 mg Mn per cubic meter of air |

## Section 3 Hazards Identification

Eye Contact: Potassium permanganate is damaging to eye tissue on contact. It may cause severe burns that result in damage to the eye.
Inhalation: Acute inhalation toxicity data are not available. However, airborne concentrations of potassium permanganate in the form of dust or mist may cause damage to respiratory tract.
Skin Contact: Contact of solutions at room temperature may be irritating to the skin, leaving brown stains. Concentrated solutions at elevated temperature and crystals are damaging to the skin.
Ingestions: Potassium Permanganate, if swallowed, may cause severe burns to mucous membranes of the mouth, throat, esophagus and stomach.

## Section 4 First Aid Measures

Eyes: Immediately flush eyes with large amounts of water for at least 15 minutes holding lids apart to ensure flushing the entire surface. Do not attempt to neutralize chemically. Seek medical attention immediately. Note to physician: Soluble decomposition products are alkaline. Insoluble decomposition product is brown manganese dioxide.
Skin: Immediately wash contaminated areas with large amounts of water. Remove contaminated clothing and footwear. Wash clothing and decontaminate footwear before reuse. Seek medical attention immediately if irritation is severe or persistent.
Inhalation: Remove person from contaminated area to fresh air. If breathing has stopped, resuscitate and administer oxygen if readily available. Seek medical attention immediately.
Ingestion: Never give anything by mouth to an unconscious or convuls ing person. If person is conscious, give large quantities of water. Seek medical attention immediately.

## Section 5 Fire Fighting Measures

**NFPA*HAZARD SIGNAL**

| | |
|---|---|
| Health Hazard | 1 = Materials which under fire conditions would give off irritating combustion products. |
| (less than 1 hour exposure) | Materials, which on the skin could cause irritation. |
| Flammability Hazard | 0 = Materials that will not burn. |
| Reactivity Hazard | 0 = Materials which in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water. |
| Special Hazard | OX = Oxidizer |

***National Fire Protection Association 704**

**FIRST RESPONDERS:**

Wear protective gloves, boots, goggles, and respirator. In case of fire, wear positive pressure breathing apparatus. Approach site of incident with caution. Use Emergency Response Guide NAERG 96 (RSPA P5800.7). Guide No. 140.

**FLASHPOINT** None

**FLAMMABLE OR EXPLOSIVE LIMITS** Lower: Nonflammable Upper: Nonflammable

**EXTINGUISHING MEDIA** Use large quantities of water. Water will turn pink to purple if in contact with potassium permanganate. Dike to contain. Do not use dry chemicals, $CO_2$, Halon® or foams.

## Section 5 Firefighting Measures (cont.)

**SPECIAL FIREFIGHTING PROCEDUREDS** If material is involved in fire, flood with water. Cool all affected containers with large quantities of water. Apply water from as far a distance as possible. Wear self-contained breathing apparatus and full protective clothing.

## Section 6 Accidental Release Measures

**STEPS TO BE TAKNE IF MATERIAL IS RELEASED OR SPILLED**

Clean up spills immediately by sweeping or shoveling up the material. Do not return spilled material to the original container. Transfer to a clean metal drum. These wastes must be deactivated by reduction. To clean floor, flush with abundant quantities of water into sewer, if permitted by Federal, State and Local regulations. If not permitted, collect water and treat chemically (Section 13).

**PERSONAL PRECAUTIONS**

Personnel should wear protective clothing suitable for the task. Remove all ignition sources and incompatible materials before attempting clean up.

## Section 7 Handling and Storage

**WORK/HYGENIC PRACTICES**

Wash hands thoroughly with soap and water after handling potassium permanganate, and before eating or smoking. Wear proper protective equipment. Remove contaminated clothing.

**VENTILATION REQUIREMENTS**

Provide sufficient area or local exhaust to maintain exposure below the TLV-TWA.

**CONDITIONS FOR SAFE STORAGE**

Store in accordance with NFPA 430 requirements for Class II oxidizers. Protect containers from physical damage. Store in a cool, dry area in closed containers. Segregate from acids, peroxides, formaldehyde and all combustible, organic or easily oxidizable materials including antifreeze and hydraulic fluid.

## Section 8 Exposure Controls/Personal Protection

**Respiratory Protection:**
In the case where overexposure may exist, the use of an approved NIOSH/MSHA dust respirator or an air-supplied respirator is advised. Engineering or administrative controls should be implemented to control dust.

**Eye Protection:**
Faceshield, goggles, or safety glasses with side shields should be worn. Provide eyewash in working area.

**Protective Gloves:**
Rubber or plastic gloves should be worn.

**Other Protective Clothing or Equipment:**
Regular work clothing covering arms and legs and a rubber or plastic apron should be worn.

## Section 9 Physical/Chemical Characteristics

**Appearance and Odor:** Dark purple solid with a metallic luster, odorless

**Boiling Point, 760 mm Hg:** N/A

**Vapor Pressure (mm Hg):** N/A

**Solubility in % By Solution:** 6% at 20°/c *68°F), and 20% at 65°C (149°F)

**Percent Volatile by Volume:** Not volatile

**Evaporation Rate (Butyl Acetate = 1):** N/A

**Melting Point:** Starts to decompose with evolution of oxygen ($O_2$) at temperatures above 150°C (302°F). Once initiated, the decomposition is exothermic and self-sustaining.

**Oxidizing Properties:** Strong oxidizer

**Specific Gravity:** 2.7 @ 20°C (68°F)

**Vapor Density (AIR=1)** N/A

## Section 10 Stability and Reactivity

**Solubility:** Under normal conditions, the material is stable.

**Conditions to avoid:** Contact with incompatible materials or heat (>150ºC/302ºF).

**Incompatible Materials:** Acids, peroxides, formaldehyde, anti-freeze, hydraulic fluids, and all combustible organic or readily oxidizable inorganic materials including metal powders. With hydrochloric acid, toxic chlorine gas is liberated.

**Hazardous Decomposition Products:** When involved in fire, potassium permanganate may liberate corrosive fumes.

**Conditions Contributing to Hazardous Polymerization:** Material is not known to polymerize.

## Section 11 Toxicological Information

Potassium permanganate: Acute oral $LD_{50}$(rat) = 780 mg/kg Male (14 days); 525 mg/kg Female (14 days)
The fatal adult human dose by ingestion is estimated to be 10 grams. (Ref. Handbook Of Poisoning: Prevention, Diagnosis & Treatment, Twelfth Edition)

**EFFECTS OF OVEREXPOSURE**

Acute Overexposure

Irritating to body tissue with which it comes into contact.

Chronic Overexposure

No known cases of chronic poisoning due to potassium permanganate have been reported. Prolonged exposure, usually over many years, to heavy concentrations of manganese oxides in the form of dust and fumes, may lead to chronic manganese poisoning, chiefly involving the central nervous system.

Carcinogenicity

Potassium permanganate has not been classified as a carcinogen by OSHA, NTP, IARC.

Medical Conditions Generally Aggravated by Exposure

Potassium permanganate will cause further irritation of tissue, open wounds, burns or mucous membranes.

Registry of Toxic Effects of Chemical Substances
RTECS #SD6476000

## Section 12 Ecological Information

**Entry to the Environment**
Potassium permanganate has a low estimated lifetime in the environment, being readily converted by oxidizable materials to insoluble MANGANESE DIOXIDE ($MnO_2$).

**Bioconcentration Potential**
In non-reducing and non-acidic environments $MnO_2$ is insoluble and has a very low bioaccumulative potential.

**Aquatic Toxicity**
Rainbow trout, 96 hour $LC_{50}$: 1.80 mg/L
Bluegill sunfish, 96 hour $LC_{50}$: 2.3 mg/L

## Section 13 Disposal Considerations

**Deactivation of D001 Ignitable Waste Oxidizers by Chemical Reduction**

Reduce potassium permanganate in aqueous solutions with sodium thiosulfate (Hypo), or sodium bisulfite or ferrous salt solution. The bisulfite or ferrous salt may require some dilute sulfuric acid to promote rapid reduction. If acid was used, neutralize with sodium bicarbonate to neutral pH. Decant or filter, and mix the sludge with sodium carbonate and deposit in an approved landfill. Where permitted, the sludge can be drained into sewer with large quantities of water. Use caution when reacting chemicals. Contact Carus Chemical Company for additional recommendations.

## Section 14 Transport Information

**U.S. Department of Transportation Information:**

Proper Shipping Name: 49 CFR 172.101……..Potassium Permanganate
ID Number: 49 CFR 172.101……..UN 1490
Hazard Class: 49 CFR 172.101……..Oxidizer
Division: 49 CFR 172.101……..5.1
Packaging Group: 49 CFR 172.101……...II

## Section 15 Regulatory Information

**TSCA** Listed in the TSCA Chemical Substance Inventory

**CERCLA** **Hazardous Substance**
Reportable Quantity: RQ – 100 lb……..40 CFR116.4; 40 CFR302.4

**RCRA** Oxidizers such as potassium permanganate meet the criteria of ignitable waste. 40 CFR 261.21

**SARA Title III Information**

Section 302 Extremely hazardous substance: Not listed
Section 311/312 Hazard categories: Fire, acute and chronic toxicity
Section 313 CAIROX® potassium permanganate contains 97% manganese compounds as part of the chemical structure (manganese compounds CAS Reg. No. N/A) and is subject to the reporting requirements of Section 313 of Title III, Superfund Amendments and Reauthorization Act of 1986 and 40 CFR 372.

| | | |
|---|---|---|
| **State Lists** | Michigan Critical Materials Register: | Not listed |
| | California Proposition 65: | Not listed |
| | Massachusetts Substance List: | 5 F8 |
| | Pennsylvania Hazard Substance List: | E |
| **Foreign Lists** | Canadian Domestic Substances List (DSL) | Listed |
| | Canadian Ingredient Disclosure List | Listed |
| | European Inventory of Existing Chemical Substances (EINECS) | 2317603 |

## Section 16 Other Information

| | |
|---|---|
| NIOSH | National Institute for Occupational Safety and Health |
| MSHA | Mine Safety and Health Administration |
| OSHA | Occupational Safety and Health Administration |
| NTP | National Toxicology Program |
| IARC | International Agency for Research on Cancer |
| TSCA | Toxic Substances Control Act |
| CERCLA | Comprehensive Environmental Response, Compensation and Liability Act of 1980 |
| RCRA | Resource Conservation and Recovery Act |
| SARA | Superfund Amendments and Reauthorization Act of 1986 |
| PEL-C | OSHA Permissible Exposure Limit-OSHA Ceiling Exposure Limit |
| TLV-TWA | Threshold Limit Value – Time Weighted Average (American Conference of Governmental Industrial Hygienists) |

# CAIROX®
# potassium permanganate

## MATERIAL SAFETY DATA SHEET



Chithambarathanu Pillai (S.O.F.)
May 2000

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# TREATABLILITY STUDY WORK PLANS
# SANTA SUSANA FIELD LABORATORY
# VENTURA COUNTY, CALIFORNIA

## *APPENDIX C*

**CHARACTERIZATION OF THE MICROBIAL POPULATIONS FROM FRACTURED ROCK CORES**

**Prepared For:**

**THE BOEING COMPANY**
**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
**and**
**UNITED STATES DEPARTMENT OF ENERGY**

**Prepared By:**

**Dr. Gláucia Lima, PhD**
**Amanda Pierce, Msc**
**Beth Parker, PhD**

**June 2009**

***Characterization of the Microbial Populations from Fractured Rock Cores***
***Santa Susana Field Laboratory, Ventura County, California – USA***

**Prepared by:** ***Dr. Gláucia Lima, PhD, Amanda Pierce, Msc, Beth Parker, PhD***

**Prepared for:** ***The Boeing Company, NASA and DOE***
***Santa Susana Field Laboratory – Treatability Study Plan – Addendum***

**Date:** ***May 29, 2009***

## INTRODUCTION

The purpose of this document is to outline the goals, objectives and to describe the materials and methods that are being applied for rock core crushing, DNA extraction and molecular biology analyses on rock core samples obtained from boreholes C12, C13, C14 and C15 from SSFL, California. This will provide information on the indigenous microbial community in a level of detail that has yet to be found in the scientific literature. This has relevance to the assessment of cleanup technology options, particularly in-situ microbial technologies, for the SSFL site.

There is abundant evidence from extensive groundwater and rock core sampling that TCE degradation occurs in the Chatsworth Formation. Historical aqueous concentration data from monitoring wells indicate the presence of cDCE and minor tDCE, 1,1-DCE, and some vinyl chloride (VC) and ethene in the groundwater (Hurley 2003; Pierce 2005). The main TCE degradation product is cis-DCE, which was detected in 42 of 122 wells sampled at the site. CSIA analyses (Compound Specific Isotope Analysis) show that the existence of cis-DCE is attributable to microbially mediated processes (Pierce 2005). Redox conditions indicated by measurements on groundwater samples by Pierce (2005) show predominantly Fe(III)-reducing conditions with local occurrences of $NO_3^{2-}$-, Mn(IV)-, $SO_4^{2-}$-reduction, and methanogenesis. Rock core samples have also been analyzed showing the existence of TCE daughter products within the rock matrix (Hurley 2003; Hurley et al. 2007).
The results of Hurley (2003) and Pierce (2005) suggest that microbial reductive dechlorination is a major degradation pathway in groundwater samples. Lab microcosm studies by Darlington et al. (2008) support this conclusion of microbial production of cis-DCE but, in contrast to the field study of Pierce (2005), no apparent complete dechlorination due to microbial processes was indicated. Both the field and microcosm studies suggest that abiotic processes cause some complete dechlorination and this may account for the minimal occurrences of acetylene measured in the field samples.

The lab microcosm studies by Darlington et al. (2008) were performed as batch tests using crushed rock samples and water from wells, both obtained from SSFL. These experiments were set up as live and autoclaved microcosms. They used samples from the microcosms actively degrading TCE and demonstrated that a *Pseudomonas* sp. was possibly the microorganism responsible for TCE to cis-DCE pathway. Darlington et al. (2008) suggested that iron-bearing minerals in the Chatsworth Formation could be responsible for abiotic degradation of TCE and cis-DCE, and they estimated the extent of this transformation to be limited to 25%.

The long term sampling of monitoring wells at the site and other evidence, such as lack of TCE or degradation products at seeps, suggests that complete degradation of TCE is likely occurring in many areas and that this may be an important influence on TCE attenuation. The possibilities that biotic pathways, in addition to abiotic pathways are causing complete dechlorination may be important and the rock core microbial studies described here are intended to elucidate the microbial community so that such possibilities can be further considered. Also, by elucidating the natural microbial community, the effect of enhancement of degradation through remedial amendments can be better assessed.

## OBJECTIVES

The objective of the present work is the characterization of the indigenous microbial communities through molecular biology tools (MBTs), utilizing the DFN approach in order to determine the spatial distribution of microorganisms in fractures and/or in the matrix pore spaces and their role in contaminant attenuation at the Santa Susana Field Laboratory (SSFL), Ventura County, California. Investigations regarding community structures will consider the presence of dechlorinating microorganisms (i.e. *Dehalococcoides* strains and others), the microbial ecology of the communities' samples and enumeration of important players through the use of molecular biology tools.

Specifically, the following questions should be addressed:

1) Is it likely, based on the identified microbial community that TCE degradation in the Chatsworth Formation can include some complete dechlorination by microbial processes?
2) Do the microbes occur only close to fractured or are they distributed throughout the rock matrix?
3) If microbes exist in the rock matrix, what are the community ecologies and how do they vary in distance away from fractures and between lithologies?
4) Is there a correlation or pattern of microbial population community and density, pore sizes, mineralogy (including organic carbon content) and contaminant concentration?

## ROCK CORE SAMPLING

Rock samples were obtained at various depths ranging from 50 to 1400 feet below ground surface (ft bgs). Sample frequency was determined according to expected contaminant concentrations and observed changes in lithology and fracture characteristics visually logged in the field. For the rock core procedure (Parker et al., 2008), boreholes were cored using an air rotary drilling technique using an HQ3 coring system, producing a 2.4-in diameter core and a nominal 3.8-in diameter borehole. The core barrels were 5 ft long. The triple tube coring systems utilize a stainless steel core barrel, an inner core barrel, and an outer core barrel all of which minimize contact of the drilling fluid or borehole water with the core. Once the inner core tube is brought to the surface, the stainless steel core sleeve is extruded using water pressure applied to one end of the core sleeve sealed with a plug. The stainless steel sleeve is split along its length to allow easy access to the core for VOC and microbial sampling, physical property sampling, and geologic logging for both structural and lithologic features.

After the rock core is retrieved and extracted from the inner core barrel, it is placed on an aluminum foil-lined PVC tray. The lithology and fractures are then logged by a geologist and the positions where the samples will be taken are determined.

## Rock Core Microbial Sample Collection Procedures

### *C-12, C-13 and C-14 Rock Core Microbial Sample Collection Procedure (Fall 2008)*

1) rock core VOC samples were chosen from the core
    a) samples adjacent to the fracture plane, at varying distances away from a fracture plane, into the unfractured matrix are selected
2) a hammer and **CLEAN** chisel were used to break each sample, a puck 2-3 inches in length, out of the core
    a) the chisel was rinsed with purge and trap grade methanol and then wiped dry with a fresh kim wipe between each break
3) selected rock core VOC samples/pucks were then chosen to split for microbial analyses
    a) the selected samples/pucks were split along their vertical axis using a hammer and CLEAN chisel
    b) the chisel was rinsed with purge and trap grade methanol and then wiped dry with a fresh kim wipe between each break
4) once split, each rock core microbial sample was wrapped in packaging used to prevent exposure to oxygen
    a) each split sample was removed from the core using a **NEW** pair of nitrile gloves and a **NEW** (torn directly from the roll still contained in the box) piece of aluminum foil
    b) the sample was wrapped in the clean sheet of aluminum foil (preferably, with the shiny side on the outside)
    c) then the sample was vacuum packed using a food grade plastic bag and a vacuum sealer
5) each sample was labeled and placed on ice or in a refrigerator until packed for shipment to the University of Guelph
6) the samples were shipped to the University of Guelph on ice
    a) the sample ID for each sample was scanned into the shipping form in the field database
    b) the bottom of a cooler was lined with a layer of ice packs, followed by a layer of bubble wrap, followed by a layer of samples
    c) the layering was repeated until the cooler is full

any extra space in the cooler is packed with bubble wrap, the chain of custody is added, and the cooler is taped shut for shipping

### *C-15 Rock Core Microbial Sample Collection Procedures (March 2009)*

The following provides a summary of the rock core microbial sample collection procedures modified in March 2009 prior to C15 coring.

1) rock core microbial samples were chosen from the core
    a) samples adjacent to the fracture plane, at varying distances away from a fracture plane, and in the unfractured matrix are selected
    b) a hammer and CLEAN chisel were used to break each sample, a puck 2-3 inches in length, out of the core; the chisel was rinsed with purge and trap grade methanol and then wiped dry with a fresh kim wipe between each break

c) information (corehole, run number distance to top of sample, distance to bottom of sample, begin sample time, end sample time, sample ID, sample type, sample position, lithologic description/comments) were recorded on the applicable field sheet

2) once the samples/pucks were broken out of the core they are packaged using the following procedure to maintain in situ REDOX conditions (presumably anoxic at depths below the watertable)
    a) the samples were removed from the core using a NEW pair of nitrile gloves and a NEW (torn directly from the roll still contained in the box) piece of aluminum foil
    b) the sample was wrapped in the clean sheet of aluminum foil (with the shiny side of the foil on the outside)
    c) a sample ID label was applied to the foil and labels indicating which end of the sample represented a fracture plane and which end is up/top are also applied to the foil
    d) the foil wrapped sample was then placed in a plastic vacuum sealable bag
    e) the bag was then placed in the vacuum sealer for nitrogen purging, evacuation, and sealing
    i) the vacuum sealer were set to run 2 nitrogen purge/evacuation cycles
    f) the sample vacuum packed in the plastic bag was then be placed in a metalized bag (oxygen barrier) and placed in the vacuum sealer
    i) the vacuum sealer was set to run 2 nitrogen purge/evacuation cycles
    ii) once evacuated and sealed, a second (duplicate) sample ID label should be applied to the outside of the metalized bag for easy scanning during packaging
3) the metalized bags were stored on ice or in a refrigerator until they are packaged for shipment to the University of Guelph
    a) each sample ID label on each metalized bag was scanned into the shipping form in the field database
    b) each metalized bag was then placed in a large plastic ziptop bag to help protect the metalized bags (the metalized bags are somewhat easily punctured)
    c) the bottom of a cooler was lined with a layer of ice packs, followed by a layer of bubble wrap, followed by a layer of sample bags
    d) the layering was repeated until the cooler is full
    e) any extra space in the cooler was packed with bubble wrap, the chain of custody is added, and the cooler was taped shut for shipping
    f) overnight shipment on ice to the University of Guelph laboratory occurs typically within 1-3 days of sample collection and preservation in the field.

By anaerobically preserving the rock samples as soon as they are lifted from the borehole, the exposure to oxygen will be minimized and recovery of microbial DNA of anaerobic microorganisms will be possible. The extracted DNA will then represent the indigenous conditions of the microbial community and it will be amplified by using sensitive molecular techniques.

## DNA EXTRACTION

After samples arrive in the laboratory at the University of Guelph, they were prepared for DNA extraction.

All rock samples were trimmed to remove the external portions of the sample that were in contact with the core barrel during extraction and also handled during packing in the field and unpacking at

the University of Guelph. All the procedure involved in the trimming and crushing were performed using sterile techniques, according to following protocol:

## Rock crushing for DNA extraction in the laboratory

1) bench tops and crushing equipment were wiped with a 70% ethanol or methanol solution
2) a propane burner was turned on to create a sterile working area
3) crushing cells and all the equipment that would have contact with the samples were washed with soap and/or sprayed with Eliminase (Fisher Cat# 04-355-32, Decon Laboratories), rinsed with deionized water and flame sterilized
4) all work from was done close to a flame and as quickly as possible to minimize die off of anaerobic microorganisms
5) bags were cut open and rock sample wrapping was opened carefully and the rock piece was placed inside a sterile stainless steel pot and trimmed using a sterile chisel
6) using a flame sterilized spatula, a trimmed piece of rock was placed inside a sterile crushing cell with the bottom plate on and then the top plate was then placed on
7) the sample was crushed using the rock crusher
8) the cell was then opened and with the flame sterilize spatula, the crushed material was transferred to a sterile 7 oz. (207 mL) Whril Pack bag (Nasco, VWR Cat# CA11216-200) and stored at -20$^{o}$C until processed

DNA has been extracted from 1 g of crushed rock using the Mo Bio PowerSoil DNA extraction kit (Cat#12888-100) following the manufacturer's protocol.

All the rock crushing procedures are performed in the sample preparation laboratory in the Axelrod building at the University of Guelph. After extraction, DNA was stored at -20$^{o}$C until processed. The DNA extraction was performed at Dr Kari Dunfield's laboratory in the Land Resource Science Department at the University of Guelph.

## PCR ASSAYS

The extracted DNA templates will amplified using the following primer sets (Table 1). PCR amplifications targeted 16S rDNA genes using universal primer sets for general Bacteria (8f/1541r) and Archaea (1Af/1100Ar). Specific primers for detection of some dechlorinating microorganisms will also be performed using primer sets for *Dehalococcoides* (Dhc1200F/Dhc1271R), *Sulfurospirilum*, *Dehalobacter*, and *Geobacter* species (other specific primer sets will be chosen for further analyses of other important groups of dechlorinators, such as the sulphate-reducing bacteria). After PCR amplification, 5 µl of PCR products will be run on 1% ethidium bromide stained agarose gels to check for the presence of amplification products.

PCR reactions and conditions on Table 2 will be used. During PCR amplifications, positive and negative controls will be used according to current laboratory practice. For positive controls, DNA templates obtained from dechlorinating cultures (gently donated by Melanie Duhamel from the University of Toronto) will be used.

**Table 1 - PCR Primers, Annealing Temperatures and Target Organisms**

| Name | Sequence | Annealing (°C) | Use | Reference |
|---|---|---|---|---|
| **1Af** | 5′-TCY GKT TGA TCC YGS CRG AG-3′ | 55 | Universal *Archaea* (PCR - 16S rDNA) | (Embley et al. 1992) + (Einen et al. 2008) |
| **1100Ar** | 5′-TGG GTC TCG CTC GTT RCC-3′ | | | |
| **8f** | 5′-AGA GTT TGA TCC TGG CTC AG-3′ | 55 | Universal *Bacteria* (PCR - 16S rDNA) | (Loffler et al. 2000;Weisburg et al. 1991) |
| **1541r** | 5′-AAG GAG GTG ATC CAG CCG CA-3′ | | | |
| **Arc340f–GC** | 5′-CGC CCG CCG CGC GCG GCG GGC GGG GCG GGG GCA CGG GGG GCC CTA CGG GGY GCA SCA G-3′ | 53.5 | *Archaea* (PCR-DGGE - 16S rDNA) | (Nicol et al. 2003) |
| **Arc519r** | 5′-TTA CCG CGG CKG CTG-3′ | | | |
| **Bac341f-GC** | 5′-CGC CCG CCG CGC GCG GCG GGC GGG GCG GGG GCA CGG GGG GCC TAC GGG AGG CAG CAG-3′ | 55 | *Bacteria* (PCR-DGGE - 16S rDNA) | (Muyzer et al. 1993) |
| **Bac534r** | 5′-ATT ACC GCG GCT GCT GG-3′′ | | | |
| **Arc931f** | 5′-AGG AAT TGG CGG GGG AGC A-3′ | 64 | >94% *Archaea* (qPCR - 16S rDNA) | (Einen et al 2008) |
| **Arcm1100r** | 5′-BGG GTC TCG CTC GTT RCC-3′ | | | |
| **Bac338f** | 5′-ACT CCT ACG GGA GGC AGC AG-3′ | 61 | >95% *Bacteria* (qPCR - 16S rDNA) | (Einen et al 2008) |
| **Bac518r** | 5′-ATT ACC GCG GCT GCT GG-3′ | | | |
| **Dhc730F** | 5′-GCG GTT TTC TAG GTT GTC-3′ | 58 | *Dhc* sp. (PCR - 16S rDNA) | (He et al. 2003;Loffler et al. 2000) Ballersdt et al 2003 |
| **Dhc1350R** | 5′-CAC CTT GCT GAT ATG CGG-3′ | | | |
| **Dhb477f** | 5′-GAT TGA CGG TAC CTA ACG AGG-3′ | 62 | *Dehalobacter restrictus Dehalobacter* strain TCA1 | (Grostern et al. 2006) |
| **Dhb647r** | 5′-TAC AGT TTC CAA TGC TTT ACG G-30′ | | | |
| **Sulf114f** | 5′-GCT AAC CTG CCC TTT AGT GG-3′ | 59 | *Sulfurospirillum multivorans, S. halorespirans* PCE-M2 *S. deleyianum* | (Duhamel et al. 2006) |
| **Sulf421r** | 5′-GTT TAC ACA CCG AAA TGC GT-3′ | | | |
| **Geo73f** | 5′-CTT GCT CTT TCA TTT AGT GG-3′ | 59 | *Trichlorobacter thiogenes, Geobacter* strain SZ | (Duhamel et al. 2006) |
| **Geo485r** | 5′-AAG AAA ACC GGG TAT TAA CC-3′ | | | |

**Table 2 - PCR Reactions and Thermalcycling Conditions**

| Primer set | Vol. (µL) | PCR buffer | $MgCl_2$ (mM) | dNTP (µL) | Taq (U) | Primers (nM) | Thermalcycling (°C/min) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Denat | Denat | Annealing | Extention | Final Extention |
| 1Af/1100Ar | 20 | 1× | 2.0 | 300 | 1.25 | 400 | 94/5m | 25 cycles | | | 72/5 |
| | | | | | | | | 94/1 | 55/1 | 72/2 | |
| 8f/1541r | 20 | 1× | 2.5 | 250 | 2.5 | 250 | 94/3m | 30 cycles | | | 72/7 |
| | | | | | | | | 94/.75 | 55/.5 | 72/1.5 | |
| Arc 340fGC/Arc519r | 25 | 1× | 1.5 | 250 | 1.0 | 310 | 94/5m | 35 cycles | | | 72/7 |
| | | | | | | | | 94/1 | 53.5/1 | 72/1.5 | |
| Bac 341fGC/534r | 25 | 1× | 2.0 | 250 | 1.25 | 360 | 94/5m | 35 cycles | | | 72/2 |
| | | | | | | | | 94/1 | 20 touchdown cycles from 65 to 55/1 + 15 cycles of 55/1 | 72/2 | |
| Dhc 730F/1350R | 20 | 1× | 1.6 | 200 | 0.5 | 210 | 94/3m | 30 cycles | | | 72/5 |
| | | | | | | | | 94/.25 | 50-58/.75 | 72/1.5 | |
| Dhb 477f/647r | 20 | 1× | 2.0 | 300 | 0.5 | 400 | 94/5 | 35 cycles | | | 72/5 |
| | | | | | | | | 94/1 | 62/1 | 72/2 | |
| Sulf 114f/421r | 20 | 1× | 2.0 | 300 | 0.5 | 400 | 94/5m | 35 cycles | | | 72/5 |
| | | | | | | | | 94/1 | 62/1 | 72/2 | |
| Geo 73f/485r | 20 | 1× | 2.0 | 300 | 0.5 | 400 | 94/5m | 35 cycles | | | 72/5 |
| | | | | | | | | 94/1 | 62/1 | 72/2 | |

## PCR-DGGE Assays

PCR-DGGE assays will be performed in order to evaluate the Bacterial fingerprints in the samples using primers (341f-GC/534r) (Table 1). After PCR amplification with the DGGE primers, 3 to 5 µl of PCR product were run on 1% agarose gel stained with ethidium bromide to verify the presence of amplification product.

DGGE assays will be performed according to established protocols (Duhamel et al. 2004;Lima et al. 2007) using denaturing gradient from 30 to 60%, 0.5×TAE buffer in a Bio-Rad equipment. After DGGE, bands representing the range of bacterial diversity in the samples will be excised, soaked overnight in double distilled and autoclaved water and re-amplified through PCR with the DGGE primer set (341f-GC/534r). PCR products will be purified using the UltraClean™ PCR Clean-Up Kit from Mo Bio (Cat# 12500-100) and sent for sequencing with the reverse primer (534r) at the Genomics Facility of the Department of Integrative Biology, University of Guelph.

## CLONING AND SEQUENCING

Cloning will be performed in a few samples of interest using the TOPO TA cloning kit from Invitrogen. Samples for cloning will be chosen according to the results of DGGE and the evidence of the presence of dechlorinating microorganisms in the samples.

Cloned plasmids will be isolated with the QIAprep® Plasmid Miniprep kit from Qiagen (Cat# 27106) according to the manufacturer's protocol. Plasmids will be sequenced at the Genomics Facility of the University of Guelph.

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# TREATABLILITY STUDY WORK PLANS
# SANTA SUSANA FIELD LABORATORY
# VENTURA COUNTY, CALIFORNIA

## *APPENDIX D*
## *BIOSTIMULATION TO TREAT CHLORINATED ETHENES IN THE CHATSWORTH FORMATION*

**Prepared For:**

**THE BOEING COMPANY**
**The NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
**and**
**The UNITED STATES DEPARTMENT OF ENERGY**

**Prepared By:**

**DAVID L. FREEDMAN**
**Professor, Clemson University**
**Department of Environmental Engineering and Earth Sciences**
**L. G. Rich Environmental Research Laboratory**
**342 Computer Court**
**Anderson, SC 29625**

**June 2009**

# Laboratory Evaluation of Biostimulation to Treat Chlorinated Ethenes in the Chatsworth Formation, Santa Susana Field Laboratory, Ventura County, California

*A Work Plan Submitted to:*

**MWH, Inc.**

**2121 N. California Blvd, Suite 600**

**Walnut Creek, CA 94596**

*Submitted by:*

**David L. Freedman**
Professor, Clemson University
Department of Environmental Engineering and Earth Sciences
L. G. Rich Environmental Research Laboratory
342 Computer Court
Anderson, SC 29625
*phone:* (864) 656-5566 *fax:* (864) 656-0672 *e-mail:* dfreedm@clemson.edu

*Administrative Address:*
**Sponsored Programs Administration**
Brackett Hall, Box 345702
Clemson, SC 29634-5702
*phone:* (864) 656-2424 *fax:* (864) 656-0881

*Date Submitted:* May 18, 2009

## 1.0 Background

MWH has identified enhanced biological reduction as one of the in situ mass transformation technologies worthy of further consideration for potential deployment at the Santa Susana Field Laboratory (SSFL). The purpose of this work plan is to outline two stages of testing at the laboratory scale that will provide the information needed to assess the effectiveness, implementability and cost of enhanced biological reduction in the feasibility study to be performed for the SSFL.

Field and laboratory evidence (2) strongly supports the conclusion that reductive dechlorination of trichloroethene (TCE) to *cis*-1,2-dichloroethene (cDCE) is an on-going process at SSFL. Natural organic matter in the groundwater and/or sandstone provides the electron donor needed for this process. Using samples from microcosms that actively reduced TCE to cDCE, Darlington (1) enriched for the dechlorinating microbes by transferring them to a defined mineral salts medium and supplying hydrogen as the electron donor and acetate as a carbon and energy source. Analysis of the enrichment culture by denaturing gradient gel electrophoresis suggested that a *Pseudomonas* sp. was most closely associated with dechlorination of TCE to cDCE.

At SSFL, the extent of further biotic reduction of cDCE to vinyl chloride (VC) and ethene appears to be limited. Only trace levels of VC and ethene have been detected in field samples. In microcosms that exhibited robust reductive dechlorination of TCE to cDCE, no significant further reductive dechlorination was observed (2). Two conditions likely explain the absence of reductive dechlorination beyond cDCE. First, reductive dechlorination of cDCE to ethene generally requires redox levels (e.g., less than -100 mV) that are lower than what is typical at most sampling locations at SSFL. Although the amount of naturally occurring biodegradable organics appears to be sufficient to support TCE reduction to cDCE, it is not sufficient to create the lower redox environment generally associated with high rates of cDCE reductive dechlorination. Second, it is likely that the microbes required for high rates of cDCE reduction to ethene, i.e., *Dehalococcoides*, are either lacking in the SSFL subsurface, or are present in extremely low numbers. Since these microbes thrive best under low redox conditions, the absence of *Dehalococcoides* activity is expected. Unless a population of *Dehalococcoides* develops, significant mass destruction of TCE and cDCE by reductive dechlorination to ethene is not likely to occur at SSFL.

Biostimulation is one of the most common forms of enhanced biological reductive dechlorination that is used to overcome the limitations described above. Biostimulation involves the addition of a substrate to the subsurface where it undergoes fermentation and generates hydrogen, which is generally regarded as the universal electron donor for chlororespiration. Acetate is also a by-product of the fermentation process. Although acetate has limited usefulness as an electron donor for reductive dechlorination of cDCE and VC, it is a required source of carbon for growth of *Dehalococcoides*, so its formation during fermentation is also a desirable outcome. A wide variety of substrates are available for use in biostimulation, including organic acids (e.g., lactate), carbohydrates (e.g., corn syrup or molasses), and emulsified vegetable oil. Some substrates are "fast-acting," i.e., they undergo rapid fermentation and release high levels of hydrogen, while others are "time-release," i.e., they undergo slow rates of hydrolysis and fermentation and therefore release hydrogen over longer periods of time and at lower concentrations. The latter

are preferred for sites where remediation is expected to take several years or longer, in order to avoid addition of substrate at frequent intervals.

In addition to reductive dechlorination, a combination of abiotic and biotic transformation processes may be a significant fate process for chlorinated ethenes at SSFL. Darlington et al. (2) demonstrated the conversion of $^{14}$C-labeled cDCE (as well as TCE) to soluble products and $^{14}CO_2$ in autoclaved microcosms. In live microcosms, $^{14}CO_2$ was the predominant product from [$^{14}$C]cDCE and [$^{14}$C]TCE. Darlington (1) speculated that iron-containing minerals in the Chatsworth sandstone are responsible for the abiotic transformation of cDCE and TCE; microbes then complete the transformation by oxidizing the products to $CO_2$. In those experiments, however, the extent of transformation was limited to approximately 25% or less of the cDCE. The reason for this limitation was not evaluated. One possibility is that the transformation capacity of the minerals was due to a lack of reductant that may be required to re-reduce them to an active state. A growing body of evidence suggests that abiotic transformation of chlorinated ethenes can be facilitated by producing low redox conditions and biostimulation can be a cost-effective way of achieving this.

Although biostimulation is used increasingly at sites contaminated with chlorinated ethenes, this approach has not yet gained as widespread adoption at sites with fractured rock. This type of environment poses a significantly greater challenge to distribution of the electron donor. Nevertheless, biotic reductive dechlorination may still be a feasible approach. Reductive dechlorination activity may be beneficial in at least two ways. First, the potential exists for the development of a biofilm in the fractures where the majority of the groundwater flows. Chlorinated ethenes that diffuse out of the rock matrix will be subjected to reductive dechlorination as long as a sufficient supply of electron donor can be maintained. A time-release substrate that adsorbs to the sandstone should be used, to prevent it from being easily flushed by groundwater flow through the fracture network. Although activity in the fractures may not impact the majority of the mass of chlorinated ethenes found in the rock matrix, it could serve to prevent any further migration of the compounds as they diffuse out. Furthermore, while the likelihood of microbes penetrating significantly into the rock matrix is small, this possibility should not be ruled out entirely. Second, as mentioned above, the creation of highly reducing conditions may facilitate the transformation of cDCE and TCE via abiotic pathways that, combined with microbial activity, yield $CO_2$ and $Cl^-$ as ultimate end products.

One limitation to a remediation process that yields $CO_2$ and $Cl^-$ as products is the difficulty in documenting the process in situ. An emerging tool for this purpose is monitoring for the enrichment of $\delta^{13}C$. Measurement of $\delta^{13}C$ has become increasingly common to ascertain the extent of biodegradation. However, it is less commonly used for processes that involve abiotic transformation such as the one envisioned for the SSFL. Obtaining data on $\delta^{13}C$ enrichment in a laboratory-controlled experiment will provide an important opportunity to document TCE and cDCE transformation in situ, via pathways other than reductive dechlorination.

## 2.0 Work Plan Objectives

The objectives of the proposed work plan address the main issues outlined above, pertaining to the feasibility of using enhanced reductive dechlorination in the SSFL subsurface:

1) Using batch microcosms, determine the effect of biostimulation on the rate of TCE reduction;

2) Using batch microcosms, determine if biostimulation enhances transformation of TCE and cDCE via pathways other than reductive dechlorination by quantifying the products formed from [$^{14}$C]TCE, as well as the extent of $\delta^{13}$C enrichment;

3) Using flow through columns, determine the extent of biofilm formation in response to biostimulation, as well as the products formed from TCE based on $\delta^{13}$C enrichment.

## 3.0 Experimental Approach

### *3.1 Microcosm Evaluation of Biostimulation and Product Formation*

The first and second objectives will be addressed in a microcosm study. Microcosms will be prepared with sandstone and groundwater from an adjacent well. The treatments will include:

- No amendments
- Biostimulation with lactate
- Biostimulation with emulsified vegetable oil
- Biostimulation with HRC-X
- Water controls
- Autoclaved controls

Lactate will be used as a positive control, i.e., nearly all of the mixed cultures that reductively dechlorinate TCE are able to use lactate as an electron donor. Emulsified vegetable oil and HRC-X are both "long-lasting" electron donors that have been used in fractured rock.

Prior to preparing the microcosms, the groundwater pH will be measured. If it is outside of the range considered optimal for reductive dechlorination (i.e., 6-8), consideration will be given to adjustment. Resazurin will be added to the groundwater (1 mg/L) to provide a colormetric indication of the redox level.

The same methods described by Darlington et al. (2) will be used to prepare the microcosms, using 160 mL glass serum bottles and Teflon-faced septa held in place with aluminum crimp caps. Samples of a rock core will be crushed at Clemson University using a hand-operated hydraulic press. The microcosms will be assembled in an anaerobic chamber. After sealing, the microcosms will be removed from the chamber and the headspaces will be purged with high purity nitrogen gas to strip out hydrogen present in the atmosphere of the anaerobic chamber. Then, TCE will be added using TCE-saturated water to an initial concentration of approximately 1 mg/L. The initial amount of electron donor added will be based on stoichiometric reduction of nitrate and sulfate (if present) plus 100 times the stoichiometric amount needed for reduction of the TCE to ethene, thereby ensuring a considerable excess.

The fate of TCE will be determined by adding [$^{14}$C]TCE to all of the treatments (approximately 0.50 μCi/bottle). To minimize the risk of adding soluble $^{14}$C contaminants from the stock solution, the [$^{14}$C]TCE will be injected into the microcosms in the gas phase after purification on a gas chromatograph, as previously described (2).

A total of 12 bottles will be prepared for each treatment. At intervals of approximately two to three months, one set of triplicate bottles will be sacrificed to determine the distribution of $^{14}$C products. The selection of sampling intervals will be based on the activity observed using routine GC headspace measurements (at approximately two week intervals).

For the second objective, a parallel set of microcosms will be prepared using the same set of treatments. However, [$^{14}$C]TCE will not be added. At the same intervals when bottles are sacrificed to determine the distribution of $^{14}$C products, bottles without the $^{14}$C added will be sent to the University of Waterloo for analysis of $\delta^{13}$C enrichment.

*Time frame:* Eighteen months

### *3.2 Evaluation of Biostimulation in Continuous Flow Columns*

The third objective will be addressed in six continuous flow columns that will contain intact pieces of sandstone, rather than crushed rock. The rock will be loaded into columns and SSFL groundwater will be pumped through at velocities selected to be appropriate in the context of the field conditions. Electron donor (selected based on the results of objective #1) will be added to five of the columns; the sixth will be used as an unamended control. The amount of donor added to each column will be varied, in order to evaluate the effect of dose on the length of time that TCE degradation can be sustained.

The columns will be monitored routinely for reductive dechlorination of TCE using 5 mL samples taken from the sampling ports. Effluent samples will be analyzed periodically for the extent of $\delta^{13}$C enrichment.

At the conclusion of column operation, samples of the rock pieces will be removed from the columns and used to determine the relative distribution of microbes on the surface of the rock versus the number that penetrated the rock matrix. Quantification of microbes will be based on the polymerase chain reaction (qPCR) using universal bacterial primers. After rinsing the surface of the rocks to remove unattached microbes, more aggressive methods will be used to extract DNA from the surface of the rock. The surface area directly exposed to the flowing groundwater will be measured in order to normalize the qPCR results in terms of the attached bacteria per $m^2$. Rock pieces will then be crushed and DNA will be extracted to estimate the extent of microbes within the rock matrix. Samples will be taken along the length of the column, to establish the distribution as a function of distance from the point of groundwater addition.

A schematic of the columns is shown in Figure 1. Each column will consist of an acrylic tube (50 cm x 3.8 cm internal diameter). The inlet will consist of 0.635 cm thick circular plate of acrylic machined and cemented to the end of the column. A 0.635 cm hole in this base plate (drilled and tapped) will serve as the inlet. A 3.5 cm diameter stainless steel screen (50 mesh)

will be placed inside the column, over the inlet hole, to retain any small pieces of rock that may block the inlet.

A flange will be machined and attached to the outlet end of the column and secured by three screws (0.318 cm). An O-ring (5.5 cm) will be placed into a machined grove in the flange to form a seal between the flange plate and the outlet plate. A 0.635 cm hole will be drilled and tapped into the outlet plate. Holes (15.9 mm) for sampling ports will be drilled at 2.4, 4.9, 10.1, 15.2, 20.1, 30.5, and 39.6 cm along the length of the column, measured from the inlet end.

The groundwater will be transferred to an 80 L Tedlar bag, which is expected to provide sufficient capacity for the duration of the experiment. Neat TCE will be added to provide 1 mg/L. The outlet of the Tedlar bag will be attached to a 40 cm length of Viton tubing. A manifold will be constructed using 0.794 mm polyethylene Tees to create six branches of tubing. A 40 cm length of the Viton tubing will extend from the manifold through six cartridges on a peristaltic pump (Cole Parmer, model #7519-06). The outlet end of the Viton tubing will be fitted over a 20-22 cm length of 0.159 cm stainless steel tubing, which will be stepped up to a 5 cm length of 0.318 cm stainless steel tubing using an adapter. This tubing will be connected to a 0.318 cm union Tee. The male branch of the tee will then be fitted with a Teflon-faced rubber septum, through which column inlet samples will be withdrawn. The outlet end of the Tee will be connected to an adapter, which will screw into a 0.635 cm stainless steel nipple (with NPT threads) and connect the valve to the inlet plate of the column.

The outlet end of the column will be fitted with a nylon male pipe adapter. A short length of tygon tubing will connect the pipe adapter to a 500 mL Erlenmeyer flask, which will collect the column effluent.

Sampling ports will be constructed by placing 0.20 cm Teflon-faced red rubber septa over the 3 mm holes and securing them in place with 5.7 cm hose clamps that will encircle the septa and the column. A 0.635 cm hole will be drilled in the hose clamps to allow access to the septa. A 3.2 cm long stainless steel needle (16 gauge) will be inserted through each septum and hole and into the center of the column. A small piece of glass wool will be placed inside the needles to minimize the chance of clogging. Female-to-male Luer stopcocks will be attached to the seven stainless steel sampling needles to seal the ports when not in use (Figure 1).

The six columns will be mounted side-by-side vertically on a frame using ring clamps. The Tedlar bag storing the groundwater will be supported by a plywood box. The bag will be placed face down to allow withdrawal of the groundwater at the low point of the bag. The testing will be conducted at room temperature, which will be recorded daily. The empty bed volume of each column will be determined by measuring the amount of water they hold without media present. The expected range is 576-581 $cm^3$ per column. The pieces of sandstone will then be added and bulk pore volumes will be measured based on the volume of water required to fill the columns.

*Time Frame:* Taking into account some method development for qPCR and allowing ample time to establish reductive dechlorination in the columns, we anticipate this effort will take 18 months.

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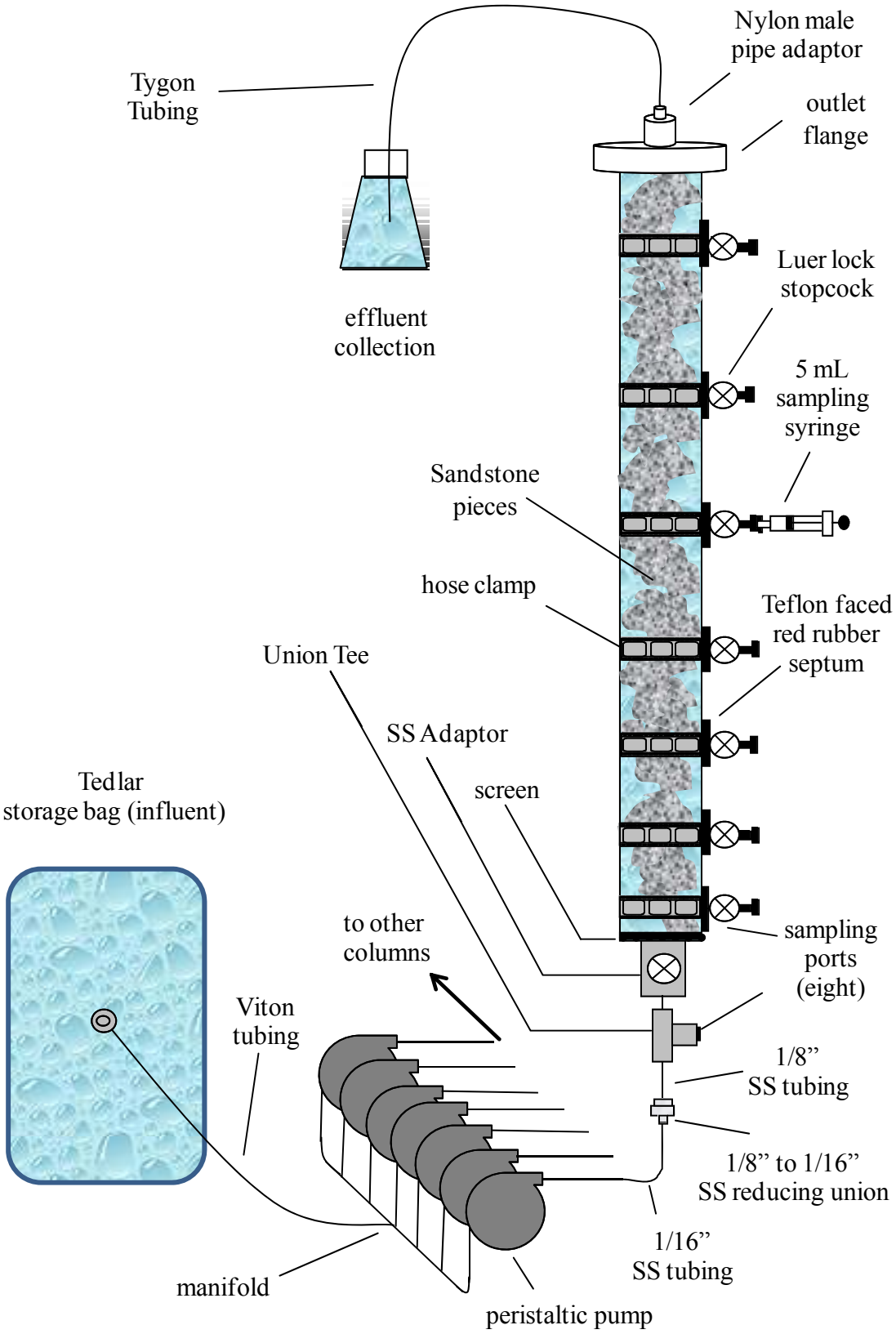



**Figure 1.** Schematic of the laboratory columns for objective #3.

# TREATABLILITY STUDY WORK PLANS
# SANTA SUSANA FIELD LABORATORY
# VENTURA COUNTY, CALIFORNIA

***APPENDIX E***
***WORK PLAN ROCK CORE THERMAL TESTING***
***SANTA SUSANA FIELD LABORATORY***

**Prepared For:**

**THE BOEING COMPANY**
**NATIONAL AERONAUTICS AND SPACE ADMINISTRATION**
**and**
**UNITED STATES DEPARTMENT OF ENERGY**

**Prepared By:**

**HALEY & ALDRICH**
**Lenexa, KS 66215-4610**

**June 2009**

# Work Plan
# Rock Core Thermal Testing
# Santa Susana Field Laboratory

## 1.0 INTRODUCTION

A bench-scale thermal treatability test will be performed on rock core samples to assist evaluation of full-scale in-situ thermal remediation for the remediation of volatile organic compounds (VOCs) in fractured sandstone at the Santa Susana Field Laboratory (SSFL). In-situ thermal remediation is being considered both for vadose zones and saturated zones in fractured sandstone at SSFL.

In-situ heating technologies enhance mass removal compared to conventional groundwater remediation and vacuum extraction technologies by heating the subsurface to evaporate pore water and volatile and semi-volatile contaminants (stripping) which are then recovered using an applied vacuum from an aboveground vapor recovery system. The performance of in-situ thermal remediation has been demonstrated via application at over 185 identified projects both in the vadose and saturated zones. These applications have provided significant insight into the performance of in-situ thermal remediation and have demonstrated that heat can be successfully and reliably applied to the subsurface to enhance mass removal compared to recovery technologies at ambient temperatures.

For saturated zones at SSFL, application of in-situ thermal remediation would consist of first dewatering the fracture system to the extent possible using conventional pumping. This dewatering step would not be required for application in vadose zones.. A dual-phase extraction system would then be used to continue removing fluids, keeping the fracture system dewatered, while the rock matrix was heated up. During the heating phase, in-situ thermal remediation would essentially be a thermally-enhanced dual-phase extraction system, with fluids being recovered using a vacuum blower. Recovered fluids would be treated aboveground using conventional vapor and liquid treatment systems. The subsurface rock could be heated via a number of alternative proven techniques, such as electrical resistance heating (ERH), radio-frequency heating, or in-situ thermal desorption (ISTD), which utilizes conductive heating. The amount of heat required to heat up a specified subsurface volume to a specified temperature could be estimated with reasonable certainty based on the results of past applications, consisting of applications applied within the vadose zone or in the saturated zone with slow groundwater flow or under dewatered conditions, because the thermal properties of rock are relatively well-defined and fairly uniform.

Although VOCs would be removed fairly quickly from the fracture system, the rate at which VOCs could be removed from the interior of the rock matrix between various fractures is uncertain. As the rock is heated up, the recovery of VOCs would be enhanced via multiple mechanisms including increased volatilization, increased desorption, and stripping/distillation. Uncertainties would include the rate of mass removal that could be achieved, the timeframe for which heating would have to be maintained, the total energy input required for remediation, and the residual VOCs that

would persist after heating was stopped. Each of these factors and the rate of mass removal from the rock matrices would largely depend on the rate of diffusion of VOCs from the rock matrices to the preferential flow channels (i.e. Chatsworth formation fracture system), which can be studied using carefully-designed tests.

Various types of site-specific testing were considered to assist evaluation of in-situ thermal remediation for SSFL. Field tests have been conducted at a large number of the 185 thermal projects performed to date, demonstrating that field tests may benefit the design of full-scale systems, but do not provide accurate estimates of full-scale effectiveness due to the small size and confined nature of typical pilot test areas. Many field pilot tests underpredict the effectiveness of full-scale application because the areas surrounding the pilot test affect the results and cause higher post-test concentrations than would be achieved if applied full-scale. The results of past field applications at other sites are also not representative for SSFL because of the unique site conditions at the site. Most thermal systems to date have been applied within or just below the vadose zone at depths down to about 100 feet. The SSFL site is characterized by the presence of contamination in fractured rock in vadose zones and down to depths of 900 feet below ground surface and hundreds of feet below the water table. Because of these site-specific characteristics, it would be very difficult to conduct a field pilot test at the SSFL site, and if conducted, a field pilot test would likely underpredict the effectiveness that could be achieved with a full-scale application.

Because of the difficulty of performing a representative field pilot test and the fact that pilot tests typically do not accurately estimate full-scale effectiveness, application of in-situ thermal remediation at SSFL will be evaluated using a series of focused bench-scale tests. The purpose of the bench-scale testing specified in this workplan will be to further understand the level to which heating enhances the recovery of VOCs and evaluate the timeframes required to remove VOC from the secondary porosity of representative rock samples from the SSFL. The bench-scale treatability study will also provided additional understanding of enhanced diffusion or other transformation processes that would occur as a result of applied heat in representative samples of fractured sandstone from the SSFL.

Specific data collection objectives of the bench test will include the following:

1) Establish baseline results for diffusion using the pilot test protocols under unheated conditions,

2) Evaluate the magnitude of diffusion or other enhanced mass transport from secondary porosity due to heating saturated bedrock,

3) Further understand the relationship of heating magnitude and duration in the rock matrix to the magnitude and proportion of VOC mass removal,

4) Develop a mass balance of VOC removal/reduction mechanisms during the heating process, and

5) Evaluate any changes in VOC composition (if any) resulting from thermal treatment.

## 2.0 EXPERIMENTAL APPROACH AND METHODS

The bench-scale study will consist of a series of two-dimensional tests designed to determine the ability to enhance removal of VOCs from the secondary porosity of fractured sandstone. Six core tests will be conducted in duplicate with ten cores heated to a specified set temperature and two held at ambient temperature as a control for comparison. Table 1 provides an overview of the core tests.

**Table 1**
**Bench Scale Study Columns**

| Core ID | | Temperature (C) |
|---|---|---|
| 1 - 2 | Control | Ambient |
| 3 – 4 | HC50 A & B | 50 |
| 5 – 6 | HC70 A & B | 70 |
| 7 - 8 | HC90 A & B | 90 |
| 9 – 10 | HC100 A & B | 100 |
| 11 - 12 | HC110 A & B | 110 |

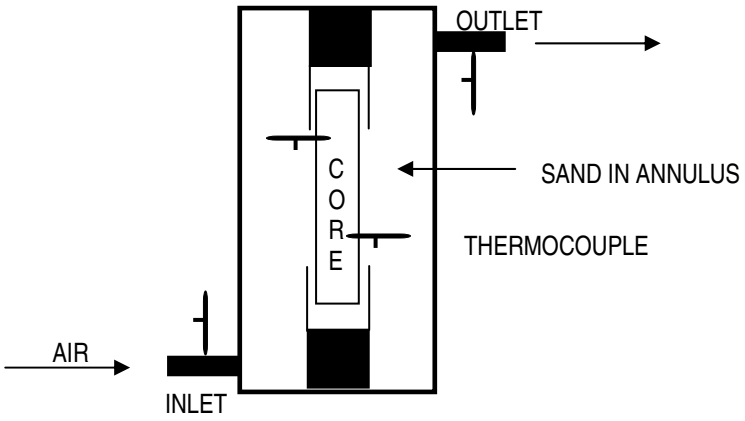
### 2.1 Sample Preparation and Handling

The test samples will consist of representative rock cores from VOC source areas that have been previously collected from the SSFL. It is expected that the diameter of the cores will be approximately 4 inches, but the tests can also be conducted with other diameters. Each core should be the same approximate length, from 3 to 8 inches. It is expected the cores will have been collected at some time preceding the bench tests and should contain TCE concentrations representative of source areas being evaluated for full-scale application of in-situ thermal remediation. After collection of the cores in the field, the cores should be wrapped and stored such that water saturation and TCE concentrations are maintained at levels as representative of the target source areas as practicable. If initial testing indicates the cores selected for bench testing do not contain appreciable VOCs, then the cores will be spiked with a known quantity or known concentration of VOCs prior to starting the diffusion tests.

At the start of the diffusion tests, the heating cores (cores 3- 12) will be transferred to a glass or equivalent testing apparatus. Inside the testing apparatus, each core will be placed upon a stand to center the core vertically. Once the core is set, the annulus of the container will be filled with 50-100 mesh clean sand and sealed with a metal lid lined with a Teflon (or equivalent non-reactive) gasket to prevent VOC vapor loss through the seals of the testing apparatus. After sealing the testing apparatus, the system will be leak tested and any leaks will be fixed prior to heating. The entire glass heating apparatus will

be held in a vertical position throughout the thermal treatability test. A schematic of the apparatus is shown in Figure 1.

**Figure 1:** Bench Test Heating Glass Apparatus Schematic




## 2.2 Experimental Setup

The thermal treatability bench test will be performed by placing the glass testing apparatus in a large oven that can be maintained at a constant temperature. The oven will accommodate vapor flow connected to sampling equipment outside the oven to facilitate analysis of the TCE desorbing from the core at specified regular intervals.

Pre-Heat Phase

The testing apparatus will be placed inside the oven where the temperature will be kept at 20°C for 2 hours. During this pre-heat time, the air flow within the annulus will be maintained at 0.1 milliliters per minute (ml/min) and the effluent from the system will be sampled and analyzed twice per hour for VOC concentrations using a pre-calibrated gas chromatograph interfaced with a mass spectrometer (i.e. GC/MS), or equivalent detector system.

Heating Phase

The oven temperature will be slowly increased from 20°C to a range of temperatures from 50°C to 110°C in increments of 4°C every two hours depending on which cores are being tested, and then held at the target temperature for the remainder of the test period. For example, cores 3 and 4 will be raised to 50°C and held for a maximum of five days. Clean compressed air will be connected to the annulus of the glass testing container passed through the test sample at a flow rate of 0.1 ml/min. The effluent vapor/condensate collection system will provide regular tracking of recovered vapors and liquids with periodic sampling for analysis. Thermocouples will be placed within the testing apparatus to allow monitoring of influent and effluent temperatures. Thermocouples will also be used to monitor the core surface temperature and the oven temperature to maintain adiabatic conditions. Figure 2 presents a schematic layout of the heating system. .During the heating phase, vapor samples will be collected every hour for

the first four (4) hours, two to four times for the next eight (8) hours, 4 to 6 times over the next 24 hours, and then three times a day for the remainder of the experiment. After reaching pre-defined temperature, the oven temperature will be held constant until vapor concentrations reach asymptotic conditions as indicated by three consecutive measurements with an absolute difference of less than 10% or a maximum time frame of five days.

If the testing facility does not have enough ovens to run all experiments simultaneously, the cores will be run sequentially starting at the lowest temperature and finishing with the highest temperature. Scheduled timeframes for sampling or the heating up phase may be adjusted slightly to accommodate less sampling during night-time hours.

Cool-Down Phase

After achieving asymptotic conditions, the oven will be turned off and allowed to equilibrate to ambient temperature (~20°C). During cool-down, vapor sampling and analysis will be continued at a frequency of twice per day until the apparatus has attained ambient temperatures for 24 hours or a maximum time frame of 3 days.

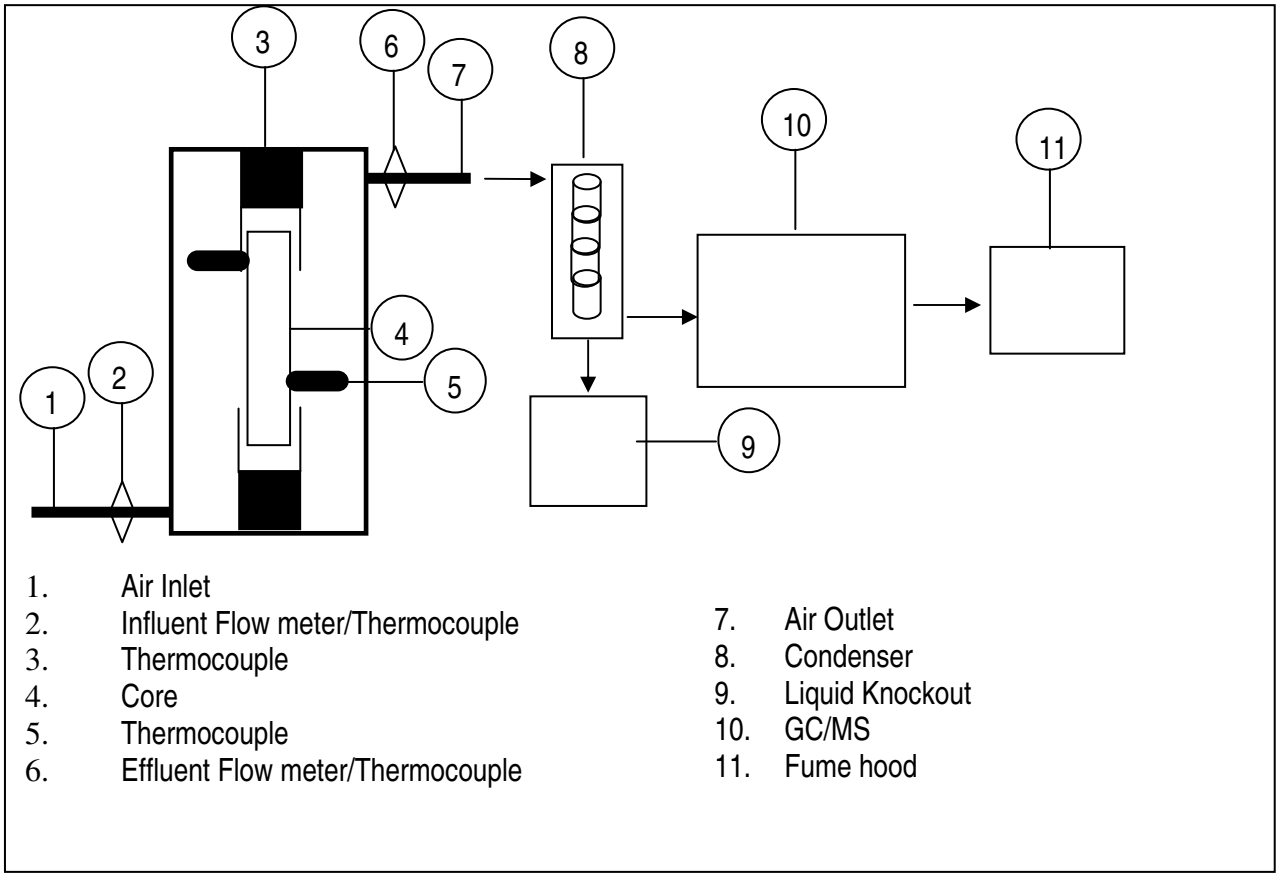



**Figure 2:** Bench Scale Testing Apparatus

All air and vapors leaving the apparatus will flow through a glass condenser. The liquid will be collected in an air tight knockout pot while the rest of the vapors flow either directly to a GC/MS or through a vapor sampling device (i.e. thermal desorption tube) for VOC analysis. Air flow leaving the GC/MS or the vapor sampling device will be vented to a fume hood.

## 2.3 Experimental Measurements

During the heating phase, ambient air will be flowing through the testing apparatus at a constant flow rate. The volume of produced condensate will be continuously monitored. The heating phase will continue until effluent vapor concentrations achieve asymptotic conditions or the maximum time frame is met upon which, the heat will be turned off. The vapor concentrations will be monitored for up to an additional 72 hours.

After the first 72 hours of the cool-down phase of the bench-scale thermal treatability study, the inlet and outlet valves will be closed and the testing apparatus moved to an area allowing the core to continue cooling and equilibrate to a constant temperature of approximately 20°C. Upon reaching ambient conditions (within +/- 5°C of 20°C), the core will be sampled according to Section 2.3.

The bench-scale study will include 12 cores, as shown in Table 1 (above). Table 2 presents the process monitoring parameters that will be collected during the study.

**Table 2**
**Measurement Criteria for Process Monitoring Parameters**

| Process Monitoring Parameter | Use in Bench-Scale Test | Measuring Instrument | Units | Range of Interest | Precision |
|---|---|---|---|---|---|
| Time | • Duration needed to raise core holder temperature.<br>• Duration for core equilibration after experiments. | Timer | Seconds | Not applicable | +/- 10 second |
| Flow Rate | • Injection and extraction air rates. | Flow Meter | Volume per minute | 0.1 ml/min | +/- 0.02 ml/min |
| Temperature | • Ambient, core, influent air, effluent air, effluent air after condensate, and convection oven temperatures | Thermocouples | Degrees Celsius | Increase from $20^o$ to 50°C-$110^o$ at a rate of $4^o$ per minute then hold constant | +/- 0.1 degree |
| Volume | • Measure incremental volume of produced effluent | Scale or volumetric | Milliliters | All milliliters | +/- 0.1 milliliter |
| Visual Observation | • Note appearance of produced effluent continually throughout condensate production | None | None, inspect effluent for globules | None | None |

Note: These parameters are data quality objectives for the bench test to be used as guidance. Modification can be made as needed.

## 2.4 Analytical Tests

Three (3) types of sample analyses will be used to perform a mass balance of the system and to indicate VOC removal from the secondary porosity of the fractured sandstone at different temperatures. The 3 types of samples to be collected as part of the SSFL Thermal Treatability Bench-Scale Test will include:

- Vapor effluent samples
- Liquid condensate samples, and;
- Solid core samples.

Effluent vapor samples will be analyzed for VOC target compounds: vinyl chloride, cis- and trans-1,2-dichloroethene, 1,1-dichloroethene, and trichloroethylene (TCE) using a GC/MS in accordance with EPA Method TO-15, or equivalent. Effluent vapor samples will be collected prior to heating, during heating as described in Section 2.2, and after treatment.

Condensate and treated core samples will be analyzed for the target VOC using EPA Method 8260B, or equivalent. Portions of each core sample will be collected for target VOC analysis post-heating and one control core will be sampled post-diffusion/pre-heating. Condensate samples from each core will be collected at the end of the thermal bench scale study to complete the mass balance.

### 2.4.1 Core Sampling

Prior to heating, one of the control cores (core 1) will be sampled to provide a baseline of VOC concentrations in the core. After the cool-down phase, cores 2-12 will be sampled (one control and all of the heating columns). Each core extracted from the testing apparatus will have a small aliquot from the midpoint of the core collected (see Figure 4 for exact sampling location) to avoid end effects. The core sample will be collected by cutting the core in half (manually) and taking a sample at the midpoint by scratching the core and collecting the dust. Each sample will be analyzed for VOC analysis by a GC/MS or equivalent detector system.

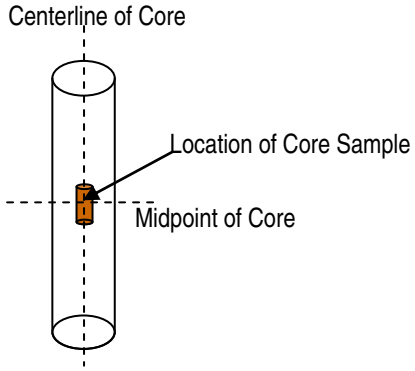



**Figure 3:** Core Sampling Location

The purpose of the core sampling will be to provide an estimate of the mass remaining in the cores prior to the diffusion tests and in each core after the diffusion tests. An alternative core sampling procedure may be selected if it would provide equal or increased accuracy compared to the procedure described above.

### 2.4.2 Quality Assurance

Sampling and laboratory quality control (QC) samples will be collected to evaluate the performance of sampling procedures and laboratory analytical procedures. Sampling and laboratory QC checks will include the collection of method blanks, matrix duplicates, and internal laboratory control samples.

**Method Blanks (Vapor, Condensate and Core Samples).** One method blank will be analyzed along with every batch of samples analyzed. The purpose of the method blank samples will be to evaluate if contaminants are introduced to the analytical system during analysis. Method blanks will be analyzed for each target VOC.

**Duplicate Samples (Core Samples Only).** One (1) duplicate sample will be collected and analyzed for each core to be heated. The duplicate sample will be collected simultaneously with a primary sample under identical conditions. The duplicate sample will be analyzed for the same analytical parameters as the primary sample.

**Internal Laboratory Control Samples (Vapor, Core and Condensate Samples).** One internal laboratory control sample will be analyzed for every 10 primary samples. The internal laboratory control sample will be prepared using NIST traceable standard reference material for each target parameter. Additional sample volume will not be required. The internal laboratory QC sample will be used instead of matrix spike/matrix spike duplicate analyses. Other laboratory QC checks will include calibration of instruments as described in the analytical methods used and analysis of surrogate and internal standards for each analysis to confirm instrument performance.

## 3.0 DATA INTERPRETATION AND REPORTING

A bench-scale study report will be prepared that describes the experimental approach and setup, work conducted and deviations from the work plan, results of various measurements and analytical sampling, and discussion of the results.

The data interpretation and evaluation will include comparing the pre- versus post-treatment VOC concentrations in the rock cores to further understand trends of VOC removed from the matrix under the test conditions. The concentration of VOCs present in the control core (core 1) samples (sacrificed prior to heating) will provide the initial VOC concentrations in the rock matrix prior to heating. The average concentrations in core samples 2 through 12 will be determined after completion of the cool-down phase will

provide the residual VOC concentrations that will potentially remain after application of an in-situ heating system.

The mass of VOCs remaining in cores 1 and 2 (not heated) will indicate characteristics of mass removal that can be achieved from the matrix under laboratory test ambient conditions (without heating). These results will then be compared to the mass of VOCs from cores 3 through 12 (heated) to indicate the drop in residual VOC concentrations after heating cores to specified temperatures.

The bench test results will help further understand characteristics of mass removal under the bench test conditions, the duration of required heating, the magnitude of energy input that will be required, and the range of residual concentrations that could remain after treatment. The results of the bench tests will be used in conjunction with data from past full-scale thermal experiences, conventional design guidelines, and past feasibility evaluations to assist in design and evaluation of possible future pilot-scale or full-scale application of in-situ thermal remediation at SSFL.